PB-242 299

INVESTIGATION OF RURAL OXIDANT LEVELS AS RELATED TO URBAN HYDROCARBON CONTROL STRATEGIES

Research Triangle Institute

Prepared for:

Environmental Protection Agency

March 1975

DISTRIBUTED BY:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

169013

PB242299

EPA-450/3-75-036
March 1975

INVESTIGATION OF RURAL OXIDANT LEVELS AS RELATED TO URBAN HYDROCARBON CONTROL STRATEGIES

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
US Department of Commerce
Springfield, VA. 22151

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-450/3-75-036

2.

3. PB 242 299

4. TITLE AND SUBTITLE
Investigation of Rural Oxidant Levels As Related to Urban Hydrocarbon Control Strategies

5. REPORT DATE
March 1975

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Research Triangle Institute
Research Triangle Park,
North Carolina 27709

10. PROGRAM ELEMENT NO.
2AC129

11. CONTRACT/GRANT NO.
68-02-1386
Task 4

12. SPONSORING AGENCY NAME AND ADDRESS
Monitoring and Data Analysis Division
Office of Air Quality Planning and Standards
Environmental Protection Agency
Research Triangle Park, N.C. 27711

13. TYPE OF REPORT AND PERIOD COVERED
Final - June 1974 to Feb.'75

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

From June 14 to August 31, 1974, a study was conducted in the Ohio Valley area to investigate high rural oxidant concentrations above the NAAQS and their possible relationship to urban hydrocarbons. Data regarding the oxidant, nitrogen dioxide, and hydrocarbon relationships were obtained by sampling from a network consisting of five rural and six urban ground stations and an instrumented aircraft. Gases sampled were O_3, NO_x, THC, CH_4, and selected hydrocarbons. Gas chromatograms of grab samples collected at three rural ground stations near Columbus and during aircraft flights were used to identify hydrocarbon species and possible tracers (e.g., C_2H_2) indicative of urban-generated pollution.

The NAAQS for photochemical oxidants (160 $\mu g/m^3$ hourly average) was exceeded twice as frequently at rural as at urban stations, with the frequency of occurrence for rural stations ranging from 10 to 20 percent of the total hourly concentration during the measurement program. Area-wide systems of high ozone concentrations were observed where the urban influence on both hydrocarbon and ozone concentrations extended from 40 to 80 kilometers (30 to 50 miles) downwind of Columbus. High ozone concentrations ($\geq 160\ \mu g/m^3$ for eight hours) were observed at all stations when the central region of a synoptic high pressure system moved into the region and persisted as long as the high pressure center remained in the immediate vicinity. No specific air trajectory could be uniformly associated with the arrival of air containing either high or low concentrations of ozone at any of the rural sites. The results of the field measurement program provide substantial support for transport of ozone precursors from urban areas to rural stations under appropriate meteorological conditions. These results also imply that the control of hydrocarbon in any individual city will not necessarily prevent the occurrence of high rural ozone concentrations in excess of the NAAQS at any given nonurban site. The implication is that the release of hydrocarbons and oxides of nitrogen from anthropogenic or biogenic sources, located in either an urban or rural area, all combine to generate appreciable quantities of ozone over wide areas.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Photochemical Air pollutants-formation and transport. Ambient ozone levels--rural and urban. Precursors of ambient ozone--hydrocarbons, nitrogen dioxide. National Ambient Air Quality Standards for ozone.	Atmospheric ozone levels Ozone formation and transport related to weather conditions	Atmospheric Photochemistry/ Air Pollution

18. DISTRIBUTION STATEMENT
Release Unlimited

19. SECURITY CLASS (This Report)
None

20. SECURITY CLASS (This page)
None

21. NO. OF PAGES
352

22. PRICE
10.00

EPA Form 2220-1 (9-73)

PRICES SUBJECT TO CHANGE

EPA-450/3-75-036

INVESTIGATION OF RURAL OXIDANT LEVELS AS RELATED TO URBAN HYDROCARBON CONTROL STRATEGIES

by

Research Triangle Institute
Research Triangle Park, N. C. 27709

Contract No. 68-02-1386 Task 4
Program Element No. 2AC129

EPA Project Officer: Robert E. Neligan

Prepared for

ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, N. C. 27711

March 1975

This report is issued by the Environmental Protection Agency to report technical data of interest to a limited number of readers. Copies are available free of charge to Federal employees, current contractors and grantees, and nonprofit organizations - as supplies permit - from the Air Pollution Technical Information Center, Environmental Protection Agency, Research Triangle Park, North Carolina 27711; or, for a fee, from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161.

This report was furnished to the Environmental Protection Agency by Research Triangle Institute, Research Triangle Park, N. C., in fulfillment of Contract No. 68-02-1386, Task 4. The contents of this report are reproduced herein as received from Research Triangle Institute. The opinions, findings, and conclusions expressed are those of the author and not necessarily those of the Environmental Protection Agency. Mention of company or product names is not to be considered as an endorsement by the Environmental Protection Agency.

Publication No. EPA-450/3-75-036

ACKNOWLEDGMENTS

This project was conducted by the Research Triangle Institute, Research Triangle Park, North Carolina, under Contract Number 68-02-1386 for the United States Environmental Protection Agency. The support of this agency is gratefully acknowledged as is the advice and guidance of the Project Officer, R. E. Neligan, and his staff.

Special acknowledgments are given to three branches of the U.S. Environmental Protection Agency--the Monitoring Applications Laboratory of the National Environmental Research Center, Las Vegas; the Chemistry and Physics and the Quality Assurance and Environmental Monitoring Laboratories of the National Environmental Research Center, Research Triangle Park. The NERC, Las Vegas, provided the aircraft and pilots for the airborne monitoring program. The Chemistry and Physics Laboratory, NERC-RTP, made available their Mobile Laboratory for in-field gas chromatographic analysis of hydrocarbons and related compounds. Recognition of the technical support of Mr. W. A. Lonnemann and Mr. R. L. Seila is acknowledged as is the advice of Dr. J. J. Bufalini and Laboratory Director, Dr. A. P. Altshuller. The Quality Assurance and Environmental Monitoring Laboratory, NERC-RTP, operated ozone analyzers in six cities located in the study area and supported the quality assurance program. Recognition of the technical support of Mr. F. J. Burmann, Mr. T. A. Hartlage, and Mr. J. C. Lang is acknowledged as is the advice of Dr. T. R. Hauser and Laboratory Director, Dr. D. S. Shearer.

Work on this project was performed by staff members of the Engineering Division and Environmental Studies Center of Research Triangle Institute under the general direction of Mr. J. J. B. Worth, Group III Vice President. Mr. Worth served as Laboratory Supervisor. Mr. C. E. Decker served as Project Leader and was responsible for coordination of the program. Staff members of Research Triangle Institute who contributed to the preparation of this report are recognized and listed in alphabetical order: Dr. W. D. Bach, Mr. C. E. Decker, Mr. W. C. Eaton, Mr. H. L. Hamilton, Mr. W. J. King, Dr. L. A. Ripperton, Mr. J. B. Tommerdahl, Dr. F. M. Vukovich, Mr. J. H. White, and Mr. J. J. B. Worth.

TABLE OF CONTENTS

Page

ACKNOWLEDGMENTS iii

LIST OF FIGURES viii

LIST OF TABLES xiv

Section

1.0 INTRODUCTION 1

2.0 STUDY PLAN 3

3.0 PROCEDURE 10

3.1 Ground Stations 10

3.1.1 Sampling Protocol 10

3.1.2 Site Locations/Description of Monitoring Stations 10

3.1.2.1 Wilmington, Ohio, (Wilmington Industrial Air Park) Station 10

3.1.2.2 Wooster, Ohio, (Wayne County Airport) Station 13

3.1.2.3 McConnelsville, Ohio, (Morgan County Airport) Station 16

3.1.2.4 DuBois, Pennsylvania, (DuBois-Jefferson Municipal Airport) Station 19

3.1.2.5 McHenry, Maryland, (Garrett County Airport Station 19

3.1.3 Air Quality Measurements 19

3.1.3.1 Instrumentation 19

3.1.3.2 Instrument Calibration and Maintenance 21

3.1.4 Data Acquisition/Reduction 24

3.1.5 Data Validation and Quality Control 27

3.2 Aircraft Measurement Program 27

3.2.1 Aircraft Flight Protocol 27

3.2.2 Aircraft System Description 28

3.2.3 Systems Operation 33

3.2.4 Instrument Calibration/Altitude Effects/Data Validation 34

3.2.4.1 Instrument Calibration 34

TABLE OF CONTENTS (Continued)

Section | Page

3.2.4.2 Altitude Effects on Instrumentation 35

3.2.4.3 Data Validation/Fly-by Comparisons/Ground Comparison Tests/Battelle Comparison Flight/Hydrocarbon Sample Contamination Test 38

3.2.4.4 Comparison of RTI Solid Phase and Bendix Gas Phase Ozone Analyzers 45

3.2.5 Data Acquisition/Reduction 45

4.0 PROGRAM SCHEDULE 50

4.1 Ground Station/Aircraft Measurement Program Schedule 50

4.2 Quality Assurance Program 53

5.0 SUMMARY OF DATA AND STATISTICS 56

5.1 Summary Statistics 56

5.2 Diurnal Patterns 63

5.3 Summary of Climatic Conditions 72

6.0 INTERPRETATION OF RESULTS 77

6.1 Examination of Ozone and Hydrocarbon Data From Aircraft Flights 77

6.1.1 Square Wave Flights 80

6.1.2 Double Box Flights 100

6.1.3 Eastern Flight of August 21, 1974 118

6.1.4 Vertical Profile Flights 121

6.1.5 Summary of Results 127

6.2 Examination of Ozone and Hydrocarbon Data From Ground Stations 129

6.2.1 Characteristics of Rural and Urban Ozone 129

6.2.2 Ozone and Hydrocarbon Data from Ground Stations 139

6.3 Relationship Between High Ozone Episodes and Synoptic Weather Conditions 147

6.3.1 Introduction 147

6.3.2 Correlation Between Pressure Systems and High Ozone 150

TABLE OF CONTENTS (Continued)

Section — Page

6.3.3 Case Studies 155
6.3.4 Discussion of Meteorological Analysis 167
6.4 Air Trajectories 172
6.5 Chemistry of Ozone Generation 177
6.6 Postulated Sequence for Ozone Generation and Destruction in Rural Areas 184
7.0 CONCLUSIONS 189
8.0 REFERENCES 191
APPENDIXES
APPENDIX A: CALIBRATION SYSTEMS/PROCEDURE 193
APPENDIX B: PERFORMANCE CHARACTERISTICS AND OPERATIONAL SUMMARIES FOR INSTRUMENTS
APPENDIX C: AIRCRAFT FLIGHT PLANS/DATA/METEOROLOGICAL SUMMARY
APPENDIX D: EVALUATION OF OZONE AND OXIDES OF NITROGEN ANALYZERS AT REDUCED PRESSURE
APPENDIX E: OPERATIONAL PROCEDURES
APPENDIX F: TRAJECTORY ANALYSIS

LIST OF FIGURES

Figure		Page
1	Location of fixed ground stations.	5
2	Square wave flight plan.	6
3	Double box flight plan.	8
4	Aerial view of Wilmington Industrial Air Park.	12
5	Aircraft, RTI, and EPA vans located on Parking Apron "C," Wilmington Industrial Air Park.	12
6	Interior view of Environmental Monitoring Laboratory showing some of the ambient air analyzers.	13
7	Interior view of Environmental Monitoring Laboratory with data acquisition system in foreground.	14
8	Aerial view of Wooster, Ohio, (Wayne County Airport) site.	15
9	Exterior view of Wooster, Ohio, (Wayne County Airport) station.	15
10	Interior view of Wooster, Ohio, (Wayne County Airport) station.	16
11	Aerial view of McConnelsville, Ohio, (Morgan County Airport) site.	17
12	Exterior view of McConnelsville, Ohio, (Morgan County Airport) station.	17
13	Interior view of McConnelsville, Ohio, (Morgan County Airport) station.	18
14	Diagram of DuBois-Jefferson Municipal Airport.	18
15	Diagram of Garrett County Airport.	20
16	Exterior view of McHenry, Maryland, (Garrett County Airport) station.	20
17	Typical data printout.	26
18	Photograph of aircraft.	29
19	Air sampling probe used on C-45 aircraft.	30
20	Block diagram of aircraft instrumentation.	31
21	Air sample bag-filling system.	32
22	Compensation factor for adjustment of Bendix $NO-NO_2-NO_x$ analyzer data for effects of altitude.	36
23	Compensation factor for adjustment of RTI ozone analyzer data for effects of altitude.	36

LIST OF FIGURES (Continued)

Figure		Page
24	System used to calibrate analyzers while airborne.	37
25	Aircraft fly-by data.	39
26	Plot of data from ozone instrument in aircraft while on ground and data from base station instrument.	40
27	Battelle comparison flight pattern.	42
28a	Data from RTI/Battelle comparison flight.	43
28b	Data from RTI/Battelle comparison flight.	44
29	Comparison data for RTI solid phase and Bendix gas phase ozone analyzers.	47
30	Results of audits of ozone analyzers at stations during period July 15-25, 1974, and August 15-21, 1974.	54
31	Mean diurnal ozone concentration at Wilmington, Wooster, and McConnelsville, Ohio, from June 14-August 31, 1974.	66
32	Mean diurnal ozone concentration at Wilmington, Ohio; DuBois, Pennsylvania; and McHenry, Maryland, from June 14-August 31, 1974.	67
33	Mean diurnal ozone concentration for Canton, Cincinnati, and Cleveland, Ohio, from June 14-August 31, 1974.	68
34	Mean diurnal ozone concentration for Columbus and Dayton, Ohio; and Pittsburgh, Pennsylvania, from June 14-August 31, 1974.	69
35	Mean diurnal ozone concentration at McHenry (Garrett County Airport) Station for 1972, 1973, and 1974.	70
36	Mean diurnal nitrogen dioxide concentration at Wilmington, Wooster, McConnelsville, Ohio; DuBois, Pennsylvania; and McHenry, Maryland, from June 14-August 31, 1974.	71
37	Mean diurnal concentration of total hydrocarbon, methane, and carbon monoxide for Wilmington, Ohio, from June 14-August 31, 1974.	73
38	Mean diurnal concentration of total hydrocarbon, methane, and carbon monoxide for Wooster, Ohio, from June 14-August 31, 1974.	74
39	Mean diurnal concentration of total hydrocarbon, methane, and carbon monoxide for McConnelsville, Ohio, from June 14-August 31, 1974.	75
40	Square wave flight pattern.	79
41	Double box flight pattern.	79

LIST OF FIGURES (Continued)

Figure		Page
42	Square wave flight of June 27, 1974.	81
43	Ozone, acetylene, and isopentane concentrations upwind and downwind of Columbus--flight of June 27, 1974.	84
44	Square wave flight of July 16, 1974.	87
45	Ozone concentration versus distance and time along the line of wind flow--flight of July 16, 1974.	89
46	Isopentane, acetylene, and carbon monoxide concentrations upwind and downwind of Columbus--flight of July 16, 1974.	91
47	Square wave flight of July 21, 1974.	93
48	Acetylene, isopentane, and carbon monoxide concentrations upwind and downwind of Columbus--flight of July 21, 1974.	95
49	Square wave flight of July 25, 1974.	97
50	Acetylene and isopentane concentrations upwind and downwind of Columbus--flight of July 25, 1974.	98
51	Double box flight of July 6, 1974.	101
52	Double box flight of July 19, 1974.	104
53	Ozone concentrations along diagonal flight legs--flight of July 9, 1974.	107
54	Suggested plume from Columbus: Flight of July 9, 1974.	1[illegible]
55	Ozone concentrations at 762 m (2500 ft) msl downwind of an urban area. Wind speed 3.6 m/sec (8 mph)--July 9, 1974.	112
56	Double box flight of July 13, 1974.	113
57	Eastern flight of August 21, 1974.	118
58	Vertical profile flights, Wilmington, Ohio, August 1, 1974.	122
59	Frequency distribution of times of maximum hourly ozone concentration--rural stations.	130
60	Frequency distribution of times of maximum hourly ozone concentration--rural stations.	131
61	Frequency distribution of times of maximum hourly ozone concentration--rural and urban stations.	133
62	Frequency distribution of times of minimum hourly ozone concentrations for rural stations.	135

LIST OF FIGURES (Continued)

Figure		Page
63	Frequency distribution of times of minimum hourly ozone concentrations for urban stations.	136
64	Comparison of frequency distributions of minimum hourly ozone concentrations for rural and urban stations.	138
65	Variation of ozone and acetylene with time of day, Ohio ground stations.	140
66	Acetylene and ozone variations, diurnal study, Wilmington, Ohio, July 18, 1974.	141
67	Acetylene and ozone variations, diurnal study, Wilmington, Ohio, July 23, 1974.	142
68	Acetylene and ozone variations, diurnal study, Wilmington, Ohio, August 14, 1974.	143
69	"Maximum Effect" curve (Ground Station Data).	148
70	"Maximum Effect" curve (Aircraft Data).	149
71	The area average value of the maximum ozone concentration (solid line) and the area average surface pressure (dashed line) versus day of the month for the latter part of the summer 1974.	151
72	The area average value of the maximum ozone concentration (solid line) and the area average surface pressure (dashed line) versus day of the month for the latter part of the summer 1973.	152
73	Nine-point running average of the data presented in figure 71.	153
74	Nine-point running average of the data presented in figure 72.	154
75	The variation of the 8-hour average value (1200 to 2000 EDT) of ozone ($\mu g/m^3$) for the period July 5-11, 1974, in the eastern United States.	156
76	A) Surface pressure (mb with only tens and units digits given) analysis (1700 EDT); B) Resultant winds; C) Mean cloud cover (tenths) (0700 to 1900 EDT) for July 6, 1974. Eight-hour average ozone values ($\mu g/m^3$) (1200-2000 EDT) indicated at each station.	157
77	A) Surface pressure (mb with only tens and units digits given) analysis (1700 EDT); B) Resultant winds; C) Mean cloud cover (tenths) (0700 to 1900 EDT) for July 8, 1974. Eight-hour average ozone values ($\mu g/m^3$) (1200-2000 EDT) indicated at each station.	159

LIST OF FIGURES (Continued)

Figure		Page
78	A) Surface pressure (mb with only tens and units digits given) analysis (1700 EDT); B) Resultant winds; C) Mean cloud cover (tenths) (0700 to 1900 EDT) for July 11, 1974. Eight-hour average ozone values (μg/m^3) (1200-2000 EDT) indicated at each station.	160
79	The variation of the 8-hour average value (1200 to 2000 EDT) of ozone (μg/m^3) for the period June 20-23, 1974 in the eastern United States.	161
80	A) Surface pressure (mb with only tens and units digits given) analysis (1700 EDT); B) Resultant winds; C) Mean cloud cover (tenths) (0700 to 1900 EDT) for July 22, 1974. Eight-hour average ozone values (μg/m^3) (1200-2000 EDT) indicated at each station.	162
81	The variation of the 8-hour average value (1200 to 2000 EDT) of ozone (μg/m^3) for the period August 25 to September 5, 1973, in the eastern United States.	164
82	A) Surface pressure (mb with only tens and units digits given) analysis (1700 EDT); B) Resultant winds; C) Mean cloud cover (tenths) (0700 to 1900 EDT) for August 27, 1973. Eight-hour average ozone values (μg/m^3) (1200-2000 EDT) indicated at each station.	165
83	A) Surface pressure (mb with only tens and units digits given) analysis (1700 EDT); B) Resultant winds; C) Mean cloud cover (tenths) (0700 to 1900 EDT) for August 29, 1973. Eight-hour average ozone values (μg/m^3) (1200-2000 EDT) indicated at each station.	166
84	A) Surface pressure (mb with only tens and units digits given) analysis (1700 EDT); B) Resultant winds; C) Mean cloud cover (tenths) (0700 to 1900 EDT) for September 4, 1973. Eight-hour average ozone values (μg/m^3) 1200-2000 EDT) indicated at each station.	168
85	Average annual hydrocarbon emissions density, 1970 tons mi^{-2}. Source: National Emissions Data Summary.	171
86(a)	Air parcel trajectories arriving at three locations for the indicated 12-hour average ozone concentrations. The triangle (Δ) indicates the 12, 24, 36 and 48-hour positions of parcels arriving at 0000 GMT; the squares (□) represent those parcels arriving at 1200 GMT.	174

LIST OF FIGURES (Continued)

Figure		Page
86(b)	Air parcel trajectories arriving at three locations for the indicated 12-hour average ozone concentrations. The triangle (Δ) indicates the 12, 24, 36 and 48-hour positions of parcels arriving at 0000 GMT; the squares (□) represent those parcels arriving at 1200 GMT.	175
86(c)	Air parcel trajectories arriving at three locations for the indicated 12-hour average ozone concentrations. The triangle (Δ) indicates the 12, 24, 36 and 48-hour positions of parcels arriving at 0000 GMT; the squares (□) represent those parcels arriving at 1200 GMT.	176
87	Population density by counties: 1970.	185
88	Tracks of centers of anticyclones at sea level, August 1973.	186

LIST OF TABLES

Table		Page
1	Pollutants measured at monitoring stations	11
2	Calibration techniques	22
3	Results of statistical comparison of the RTI solid phase instrument versus Bendix gas phase instrument	46
4	Program schedule	51
5	Listing of aircraft flights	52
6	Statistical summary of hourly ozone concentration measurements by station (June 14-August 31, 1974)	56
7	Summary of ozone data above NAAQS by station (June 14-August 31, 1974)	57
8	Statistical summary of hourly nitrogen dioxide concentration measurements by station (June 14-August 31, 1974)	57
9	Statistical summary of hourly total hydrocarbon, methane and carbon monoxide concentration measurements by station (June 14-August 31, 1974)	58
10	Cumulative frequency distributions of hourly concentration of ozone by station (June 14-August 31, 1974)	60
11	Cumulative frequency distributions of hourly concentration of nitrogen dioxide by station (June 14-August 31, 1974)	61
12	Cumulative frequency distributions of hourly concentrations of total hydrocarbon, methane, and carbon monoxide by station (June 14-August 31, 1974)	62
13	Means of hourly concentrations of ozone for each hour of day (June 14-August 31, 1974)	64
14	Means of hourly concentrations of nitrogen dioxide, total hydrocarbon, methane, nonmethane hydrocarbon, and carbon monoxide for each hour of day (June 14-August 31, 1974)	65
15	Comparison of low altitude resultant wind velocity at selected locations by month	76
16	Abstract of hydrocarbon data: Square wave flight of June 27, 1974	82
17	Abstract of hydrocarbon data: Square wave flight of July 16, 1974	88
18	Abstract of hydrocarbon data: Square wave flight of July 21, 1974	94

LIST OF TABLES (Continued)

Table		Page
19	Abstract of hydrocarbon data: Square wave flight of July 25, 1974	99
20	Abstract of hydrocarbon data: Double box flight of July 6, 1974	102
21	Abstract of hydrocarbon data: Double box flight of July 9, 1974	105
22	Wind observations, July 9, 1974	108
23	Characteristics of ozone concentration distributions by flight leg	109
24	Abstract of hydrocarbon data: Double box flight of July 13, 1974	114
25	Abstract of hydrocarbon data: Eastern flight of August 21, 1974	119
26	Abstract of hydrocarbon data: Vertical profile flight, Wilmington, Ohio, August 1, 1974	123
27	Abstract of hydrocarbon data: Vertical profile flight, Wooster and McConnelsville, Ohio, August 13, 1974	124
28	Abstract of hydrocarbon data: Vertical profile flight, Wilmington, Ohio, August 15, 1974	125
29	Summary statistics for the daily maximum ozone concentration for five rural and six urban stations	132
30	Summary statistics for the daily minimum ozone concentration for five rural and six urban stations	134
31	Abstract of hydrocarbon data: Diurnal study, Wilmington, Ohio, July 18, 1974	144
32	Abstract of hydrocarbon data: Diurnal study, Wilmington, Ohio, July 23, 1974	145
33	Abstract of hydrocarbon data: Diurnal study, Wilmington, Ohio, August 14, 1974	146
34	Concentrations of tropospheric ozone as given in more recent and extensive studies. (From Junge, "Air Chemistry and Radioactivity")[1]	179
35	Summary of simulated time-concentration profiles for propylene-NO_x chemistry[a,b]	180
36	Summary of simulated time-concentration profiles for propylene-NO_x chemistry[a,b]	181
37	Jeffries'-Sickles' reaction mechanism[a]	183

1.0 INTRODUCTION

Photochemical smog until recently has been generally considered an urban phenomenon. Control strategies and implementation plans to achieve the 1971 National Ambient Air Quality Standard (NAAQS) for photochemical oxidants [160 $\mu g/m^3$ (0.08 ppm) hourly average not to be exceeded more than once per year] have mostly been focused on cities where the smog problem has been identified.

In the late 1960's, ozone concentrations in rural areas in excess of the generally accepted range for natural surface air (0.02-0.06 ppm, average < 0.02 ppm)[1/] were measured. As a specific example, reports of damage to Christmas tree plantations in the area of Mount Storm, West Virginia, and Garrett County, Maryland, led in 1970 to air pollution studies and special oxidant measurements. Unexpectedly high oxidant[2/] and high ozone[3/] concentrations were found at the above-mentioned locations. The Environmental Protection Agency (EPA), in 1972, contracted with the Research Triangle Institute (RTI) to conduct a study of atmospheric ozone in Garrett County, Maryland, and Preston County, West Virginia.[4/] This 1972 study confirmed the earlier reports of high ozone concentrations; approximately 11 percent of 1,043 hourly measurements made at the Garrett County, Maryland, Airport during the summer of 1972 exceeded the NAAQS (160 $\mu g/m^3$). Similar findings were obtained at satellite locations located around the base stations at a radius of approximately 19 kilometers.

Analysis of synoptic meteorological data, as well as an examination of ozone wind roses for the Garrett County, Maryland, Airport led to a hypothesis that the high ozone concentrations at this location developed within particular air masses, which acquired and maintained their characteristics over broad geographic regions.

In the summer of 1973, in order to further assess the areal extent of the rural high ozone concentrations, the EPA contracted with RTI to establish a network of four monitoring sites for the measurement of ground-level ozone concentrations and to carry out airborne measurements of ozone with an instrumented twin-engine aircraft.

These four sites were located at or near McHenry, Maryland (Garrett County); Kane, Pennsylvania; Coshocton, Ohio; and Lewisburg, West Virginia. This study confirmed the hypothesis that the high rural ozone concentrations extended over a considerable area. For the summer and early fall of 1973, the NAAQS was exceeded during 15 percent of 1,663 hours at Lewisburg, West Virginia; 37 percent of 1,652 hours at McHenry, Maryland; 30 percent of 2,131 hours at Kane, Pennsylvania; and 20 percent of 1,785 hours at Coshocton, Ohio.[5/]

In an effort to obtain information that would bear on the question of whether control of hydrocarbon emissions in urban areas could cause an abatement of the high rural ozone concentrations, the EPA funded the present study, in which relationships were sought between the rural oxidant (ozone) concentrations and ozone precursors--that is, hydrocarbons and oxides of nitrogen.

Specifically, the study was to investigate the urban hydrocarbon-"downwind" ozone relationship and, if possible, to obtain information that would indicate whether hydrocarbons from one city could influence the ozone concentration of another.

2.0 STUDY PLAN

An investigation into possible relationships between urban hydrocarbon and rural oxidant concentrations was designed to determine changes in concentrations of specific atmospheric pollutants and classes of pollutants during the passage of air over and downwind of an urban area. Perturbations in ozone concentration should occur in air moving over the earth's surface from rural to urban to rural to urban areas. Hence, it could be theorized that generation of ozone downwind from the cities would be accompanied by decreases in concentrations of the oxides of nitrogen and in the more reactive hydrocarbons, both by dilution and by reaction.

2.1 Design of Study

In order to accomplish the objective set forth in section 2.0, measurements of the concentration of ozone (O_3), oxides of nitrogen (NO_x), and hydrocarbons (HC) of different reactivity must be obtained in air flowing from an urban area. To determine the changes in concentrations and in concentration ratios, measurements must be made at two or more points downwind of the urban area. Unfortunately, optimum distances (or travel times) for detecting the postulated concentration changes are not known. A further complication in designing a measurement-station array is that the normal day-to-day variations in wind direction preclude the selection of a line that, with a high degree of confidence, can be assumed to represent flow from the urban areas.

Additionally, in establishing the measurement protocol for achieving the objective, provision must be made for assuring that useful data are collected under each of several meteorological conditions. Primarily, these meteorological conditions can be separated into those providing a well-defined flow pattern and those representing stagnant conditions characterized by low wind speed with variable direction.

Based on the above considerations, two modes of measurement were employed: a network of five fixed, rural, ground-level stations and an instrumented airplane flying specified patterns. These are discussed in the following paragraphs.

2.1.1 Ground-Level Stations

Since the basic problem is the occurrence of high ozone concentrations in rural air, a network of ground stations was established in order to document occurrence of such concentrations during the observation program.

Central Ohio, specifically the city of Columbus, was selected as the key area for investigation. Of all the areas in the Ohio Valley, the vicinity of Columbus has the most uniform terrain, and synoptic wind flow should be minimally affected by local topography. Finally and most important, persistent periods of ozone concentrations in excess of the National Ambient Air Quality Standard (NAAQS) have been observed in rural air in this region.

Figure 1 shows the selected locations of fixed ground stations for the study. The station at McHenry, Maryland, provides continuity with previous studies of ozone concentration in rural areas; data have been collected at this site during the summers of 1972 and 1973. The other eastern station is at DuBois, Pennsylvania, and the remaining three stations are located at Wilmington, Wooster, and McConnelsville, Ohio. Wilmington was selected as the base station for the field measurement program which extended from June 14 to August 31, 1974. Data from these rural stations were supplemented by data from urban stations, which were operated under the auspices of the Environmental Protection Agency. These urban stations were located in Pittsburgh, Canton, Cleveland, Dayton, Cincinnati, and Columbus; their geographical locations with respect to the rural stations are shown in figure 1.

2.1.2 Airborne Measurements

Flight patterns were selected to provide for the collection of data at several distances downwind from the urban area. Two flight patterns were used. One of these (fig. 2) is a "square wave" pattern which was flown on occasions when the advective transport was predictable (i.e., windspeeds equal to or greater than 7 knots) and could be expected to persist over a 4- to 6-hour period. The pattern extends from 37 kilometers upwind of the city, in order to provide background data, and up to 185 kilometers downwind of the city. A straight path flight returns over the area covered to measure the changes with time in pollutant concentrations.

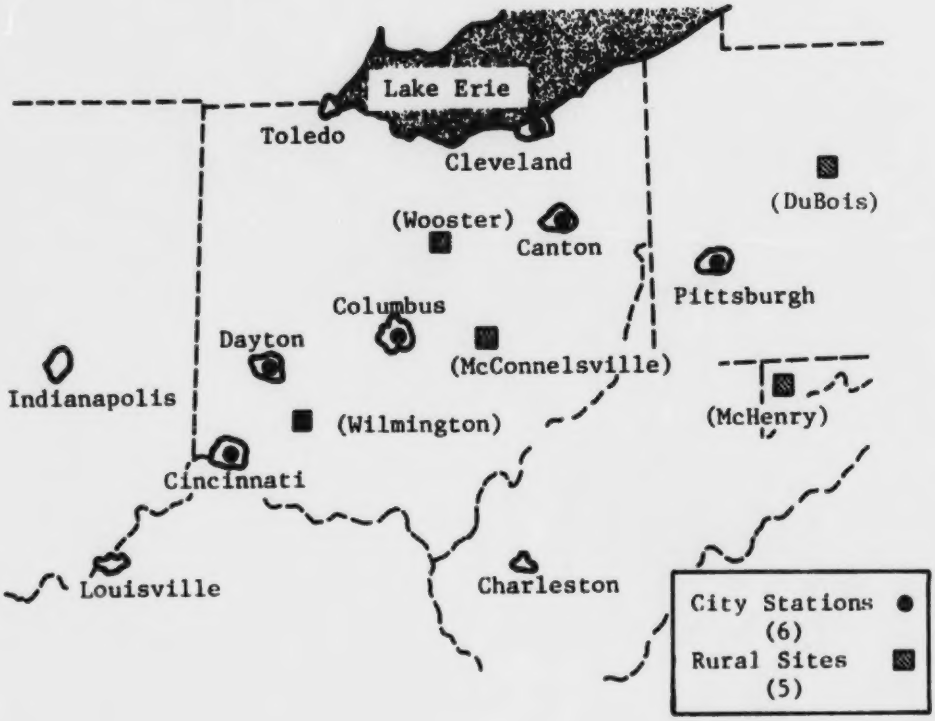

Lake Erie
Toledo
Cleveland
(DuBois)
(Wooster)
Canton
Pittsburgh
Columbus
Dayton
(McConnelsville)
Indianapolis
(McHenry)
(Wilmington)
Cincinnati
Louisville
Charleston
City Stations ●
(6)
Rural Sites ▨
(5)

Figure 1. Location of fixed ground stations.

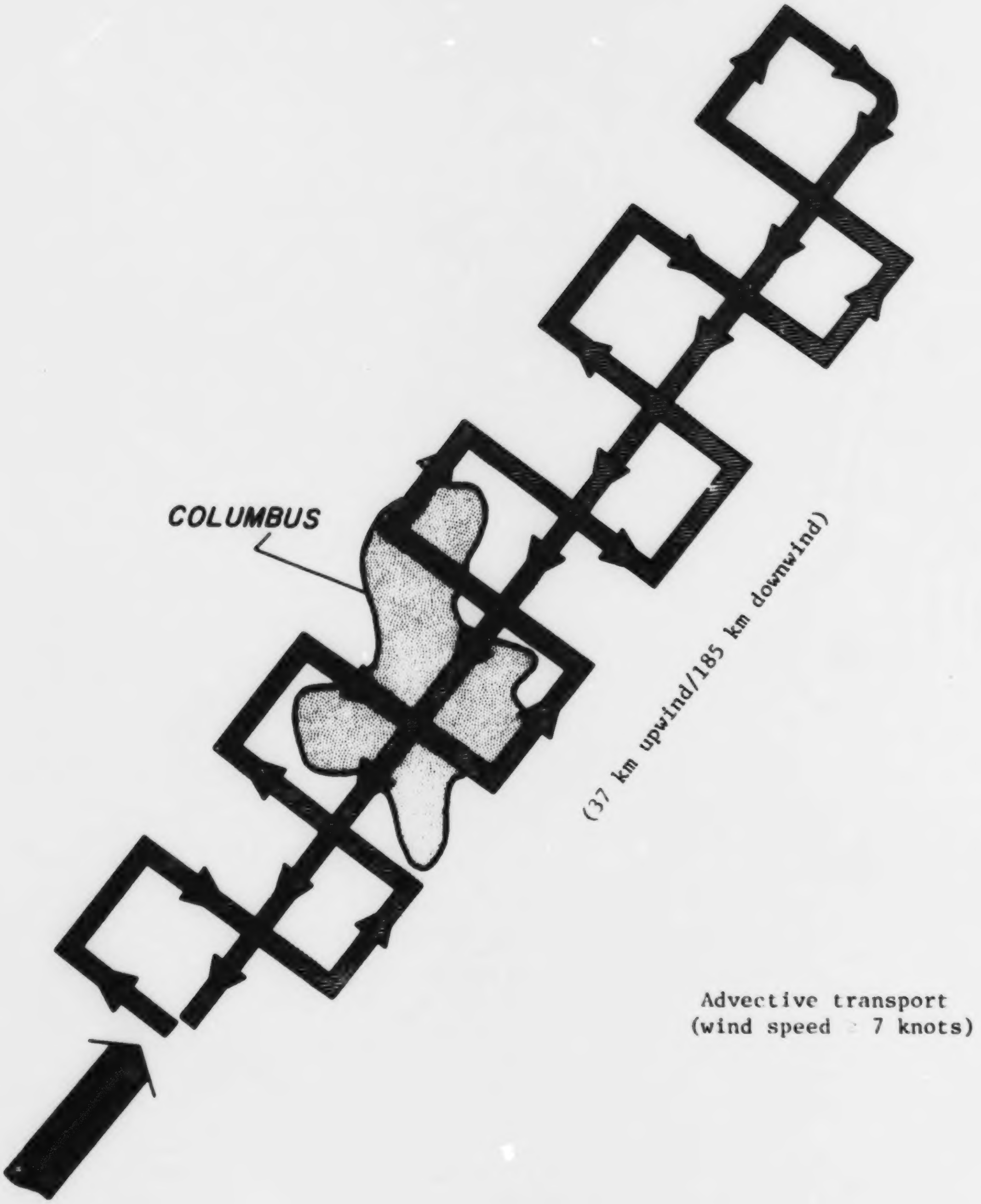

COLUMBUS
(37 km upwind/185 km downwind)
Advective transport
(wind speed ≥ 7 knots)

Figure 2. Square wave flight plan.

The second flight pattern was in the shape of a double box (fig. 3). This flight was used under stagnant air mass conditions (i.e., wind speed less than 3 knots and wind direction undefined). As shown in the figure, a diagonal path over the urban area is superimposed on a pattern of two squares. The inner square has side lengths of 46 kilometers; the outer has side lengths of 139 kilometers.

Comparison of concentration values obtained with the airplane instruments with those at the base station was made by a low-level flight over the ground station (approximate altitude of 15 meters) at the beginning and the end of each flight pattern.

The double box flight patterns retained the same orientation for all flights. The square wave pattern was oriented according to the predicted wind directions, with the long leg downwind of the urban area.

Both square wave and double box flights were made at an altitude midway between the surface and the top of the mixing layer. All flights were planned for cloud-free conditions at flight level and between flight level and the surface.

In addition to the patterned flights, certain other flights were made: 1) an eastward flight into Pennsylvania to examine the areal distribution of the ozone, 2) vertical profiles in the area of the base station (morning, midday, and evening), and 3) a flight between the three Ohio stations with vertical profiles at each station.

2.2 Analysis Procedure

The relationships between urban hydrocarbons and rural-area high ozone concentrations were investigated through study of measurements of concentrations of:

total hydrocarbon	(THC)
methane	(CH_4)
ozone	(O_3)
nitrogen dioxide	(NO_2)

selected hydrocarbons, including acetylene.*

---

*Gas chromatographic analysis of selected hydrocarbons in grab samples was provided by the Chemistry and Physics Laboratory of National Environmental Research Center, Research Triangle Park, North Carolina.

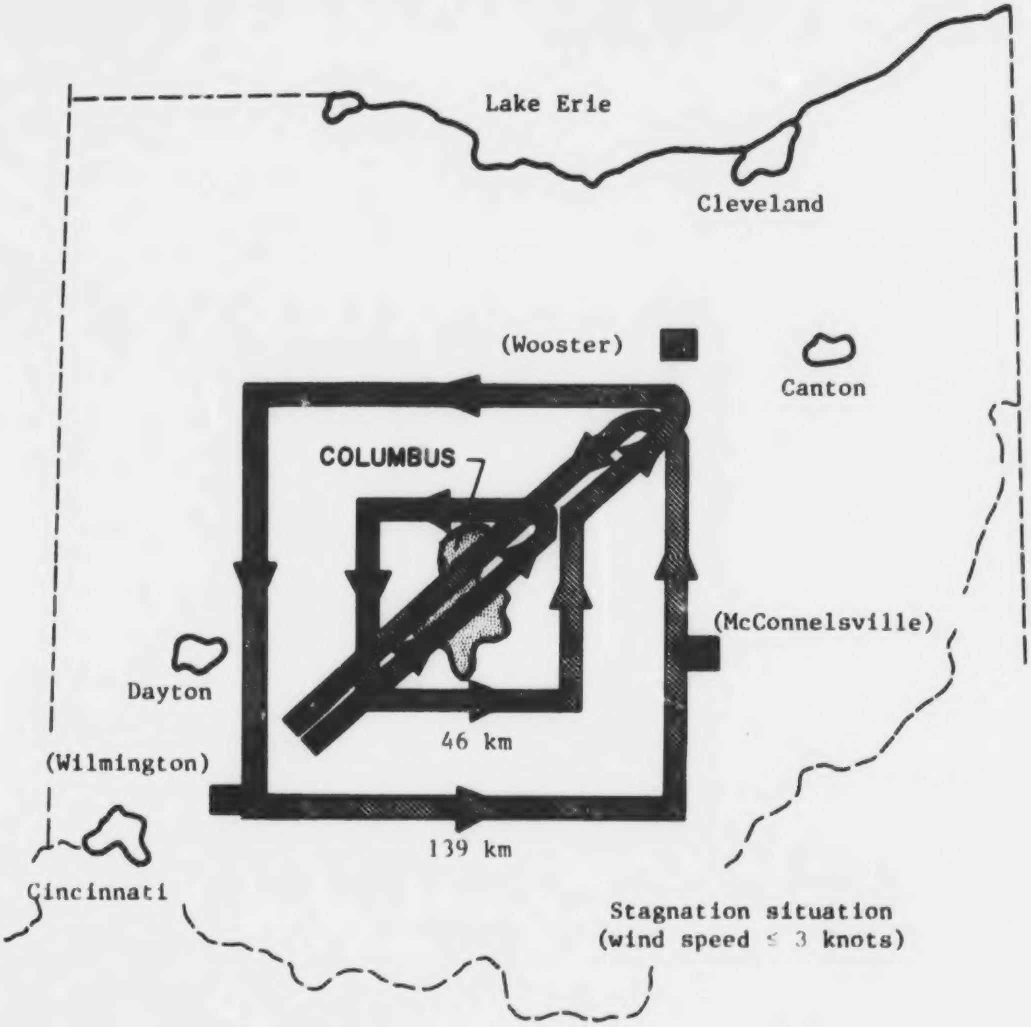

Lake Erie
Cleveland
(Wooster)
Canton
COLUMBUS
(McConnelsville)
Dayton
46 km
(Wilmington)
139 km
Cincinnati
Stagnation situation
(wind speed ≤ 3 knots)

Figure 3. Double box flight plan.

Values and ratios of concentrations of these pollution components were examined, and comparisons were made upwind, over, and downwind of Columbus, using data collected from the airplane flights. Ground station data were used to verify the occurrence of rural high concentrations of ozone and to determine concurrent concentrations of THC, CH_4, and NO_2. Gas chromatograms of grab samples from the three ground stations near Columbus were used to identify hydrocarbon species for the identification of possible tracers (e.g., C_2H_2) indicating urban-generated pollution.

The rationale for the analysis is based on the assumption that the NMHC/C_2H_2 ratio should provide an indication of the contribution by the city to the total nonmethane hydrocarbon input, and an indication of the point at which the urban pollutant input no longer has an influence or where its presence can no longer be detected. Gas chromatograms of the individual organic compounds should show whether or not the city organics, as a group of compounds, become indistinguishable from the hydrocarbon compounds in the background air entering the city. Under ideal circumstances, by comparing these ratios and concentrations obtained from the aircraft and from the ground stations with the O_3 readings, a sound judgement can be made as to whether, and if so, to what degree, the hydrocarbons of the city exert a detectable influence on O_3 concentrations in the background system.

3.0 PROCEDURE

This section describes the protocol for the ground station network, aircraft measurement program, and gas chromatographic field facility. Site locations, instrumentation, calibration, maintenance, and data-processing procedures employed in each of the above-mentioned areas are described.

3.1 Ground Stations

3.1.1 Sampling Protocol

The field measurement program was designed to measure continuously the ambient concentration of O_3, NO_2, THC, CH_4, and NMHC by difference at each of three manned stations in central Ohio, and O_3 and NO_2 at two stations--one each in Pennsylvania and in Maryland. Availability of specific hydrocarbon analyzers and the necessity of full-time field operators restricted NMHC measurements to the three stations in central Ohio. In addition to the five rural stations, the Quality Assurance and Environmental Monitoring Laboratory of the Environmental Protection Agency maintained and operated ozone analyzers at six city locations surrounding the general study area. The six cities were Canton, Cincinnati, Cleveland, Columbus, and Dayton, Ohio, and Pittsburgh, Pennsylvania. Grab samples were also collected daily at the three sites in central Ohio and sent to the Wilmington site for subsequent analysis of individual hydrocarbons by gas chromatography. Pollutants measured at each ground station are listed in table 1.

3.1.2 Site Location/Description of Monitoring Stations

The principal criteria for the selection of a monitoring station location were: 1) that the location be relatively free of natural and manmade obstructions to air movement, 2) that it be removed from anthropogenic sources of O_3 precursors, and 3) that it be readily accessible by aircraft in order to facilitate timely maintenance and routine calibration schedules. The locations selected met these criteria.

3.1.2.1 Wilmington, Ohio (Wilmington Industrial Air Park)

The Wilmington Industrial Air Park (formerly the Clinton County Air Force Base) located 6 kilometers southeast of Wilmington, Ohio, served as the base station for operations during the summer oxidant study. Four vans (i.e., RTI base station, Environmental Protection Agency

Table 1. Pollutants measured at monitoring stations

Station	Pollutants
Wilmington, Ohio*	O_3, NO_2, THC, CH_4, HC by GC**
McConnelsville, Ohio	O_3, NO_2, THC, CH_4, HC by GC**
Wooster, Ohio	O_3, NO_2, THC, CH_4, HC by GC**
McHenry, Maryland	O_3, NO_2
DuBois, Pennsylvania	O_3, NO_2
Canton, Ohio	O_3
Cincinnati, Ohio	O_3
Cleveland, Ohio	O_3
Columbus, Ohio	O_3
Dayton, Ohio	O_3
Pittsburgh, Pennsylvania	O_3

*Base Station **Grab Samples

Chemistry and Physics Laboratory Van, RTI trailer, and Rutgers University Van) and the Environmental Protection Agency Aircraft (C-45) were based there. With the exception of the Rutgers University van, which was on site for only 2 weeks in July, the facilities were operated at the base station from the middle of June until the end of August. Figure 4 shows an aerial view of the airfield and the surrounding terrain. Figure 5 is a photograph showing the C-45 aircraft, the RTI Environmental Monitoring Laboratory, and the EPA Chemistry and Physics Laboratory Van on location at Parking Apron "C", Wilmington Industrial Air Park.

The elevation of the airfield is 403 meters above mean sea level, and exposure is excellent from all directions. The airfield and hangars are leased to Overseas National Airways, which maintains a maintenance facility there. Overseas National Airways has jurisdiction over the airfield, and traffic in and out averages approximately three flights per week.

The RTI Environmental Monitoring Laboratory was used as the base station at Wilmington. It is a self-contained, 9.4-meter motorized vehicle, custom-built for air quality monitoring. It is outfitted with the latest complement of air quality monitoring instrumentation, a self-contained

Figure 4. Aerial view of Wilmington Industrial Air Park.

Figure 5. Aircraft, RTI, and EPA vans located on Parking Apron "C," Wilmington Industrial Air Park.

calibration system for each pollutant analyzer, and a digital magnetic tape recording system coupled to a minicomputer capable of online data processing and printout of real-time air quality data in concentration units and storage of the raw data on magnetic tape. The motorized van has a self-contained motor-generator for generation of electrical power, a controlled environment (heating and cooling), an a.c. voltage regulator, a glass and Teflon manifold system for passage of air samples to the monitors, a tower for mounting various meteorological sensors, and storage space for compressed air and gas tanks.

Two interior views of the vehicle are shown in figures 6 and 7.

3.1.2.2 Wooster, Ohio (Wayne County Airport)

The Wooster, Ohio, station was located at the Wayne County Airport, approximately 10 kilometers northeast of Wooster, and is 346 meters above mean sea level. Exposure is excellent from all directions. Figure 8 is an aerial view of the county airfield and the surrounding terrain.

Instrumentation and associated equipment were housed in an 2.4-by-6-meter construction trailer modified to accommodate the ambient air

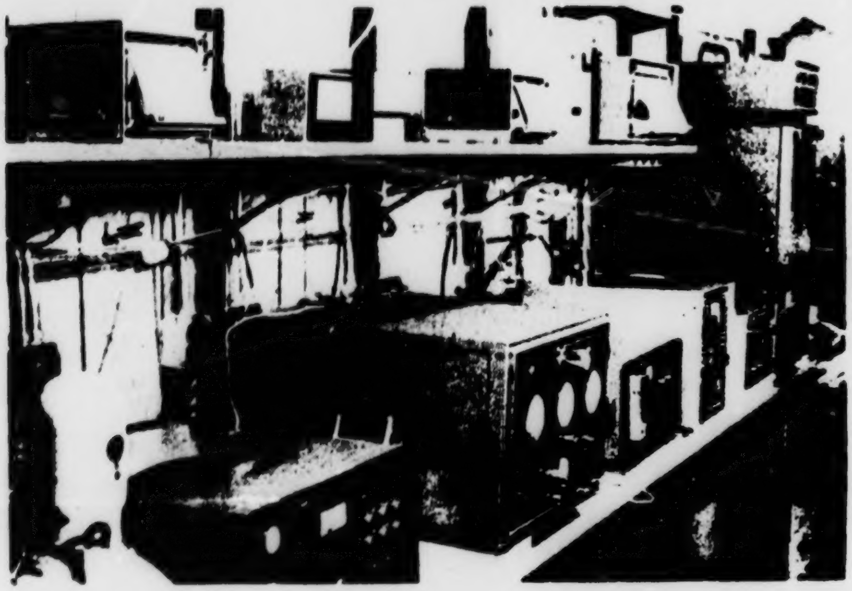


Figure 6. Interior view of Environmental Monitoring Laboratory showing some of the ambient air analyzers.

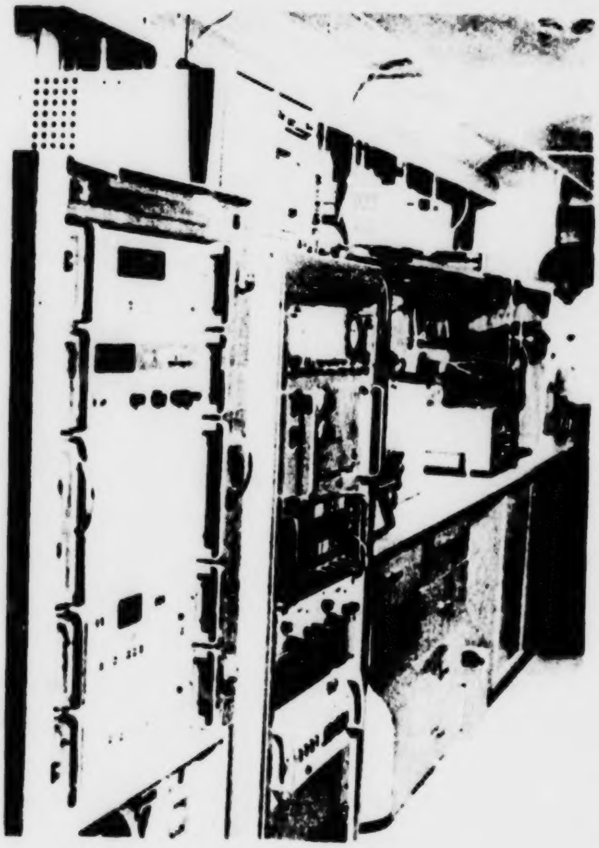


Figure 7. Interior view of Environmental Monitoring Laboratory with data acquisition system in foreground.

quality analyzers and the data-acquisition and calibration systems (fig. 9). Two air-conditioning units were installed on either end of the construction trailer to control the interior temperature to approximately 22° ± 2°C. An interior view of the station is pictured in figure 10. Ozone, NO_2, THC, and CH_4 concentrations were recorded at this station. Also, grab samples were collected twice daily--once in the morning and again in the evening. These samples were forwarded daily to Wilmington by United Parcel Service for subsequent analysis of individual hydrocarbons by gas chromatography. The ambient air inlet was located at a point 3 meters above the roofline. An all glass and Teflon inlet system with blower was used to aspirate sample air through the manifold. Each analyzer sampled directly from the manifold.

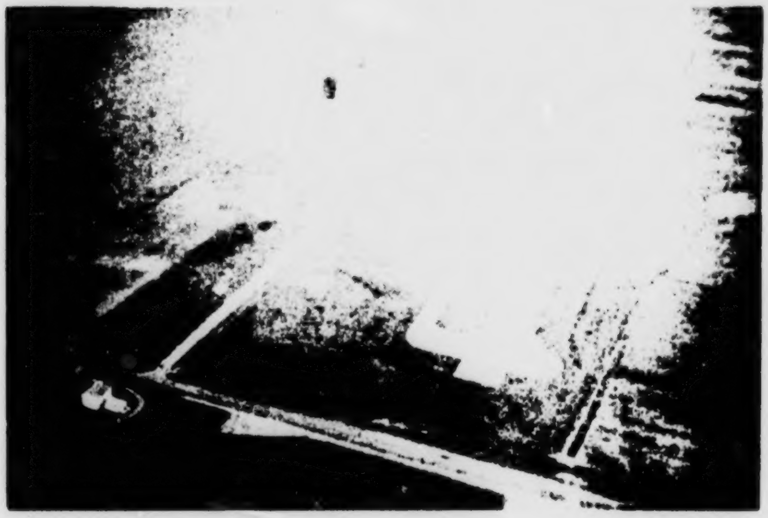


Figure 8. Aerial view of Wooster, Ohio, (Wayne County Airport) site.

Figure 9. Exterior view of Wooster, Ohio, (Wayne County Airport) station.

Figure 10. Interior view of Wooster, Ohio, (Wayne County Airport) station.

3.1.2.3 McConnelsville, Ohio (Morgan County Airport)

The McConnelsville, Ohio, station was located at the Morgan County Airport situated approximately 40 kilometers southeast of Zanesville, Ohio. The airport elevation is approximately 305 meters above mean sea level, and the site has good exposure from all directions. Due to the limited access to electric power at this site, a 2.4-by-6-meter construction trailer was located adjacent to a small building, which served as a terminal. An aerial view of the site with respect to the surrounding terrain is shown in figure 11. An exterior view of the trailer located on site is shown in figure 12. An interior view of the station is pictured in figure 13. The measured pollutants and details of the sampling station were identical to those at Wooster. Aircraft traffic into Morgan County was mainly local, small-engine planes and averaged less than three flights per week.

Figure 11. Aerial view of McConnelsville, Ohio, (Morgan County Airport) site.

Figure 12. Exterior view of McConnelsville, Ohio, (Morgan County Airport) station.

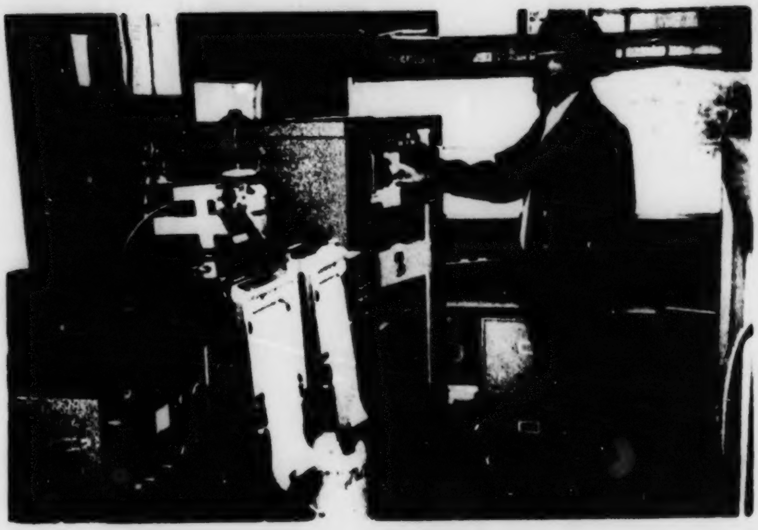


Figure 13. Interior view of McConnelsville, Ohio, (Morgan County Airport) station.

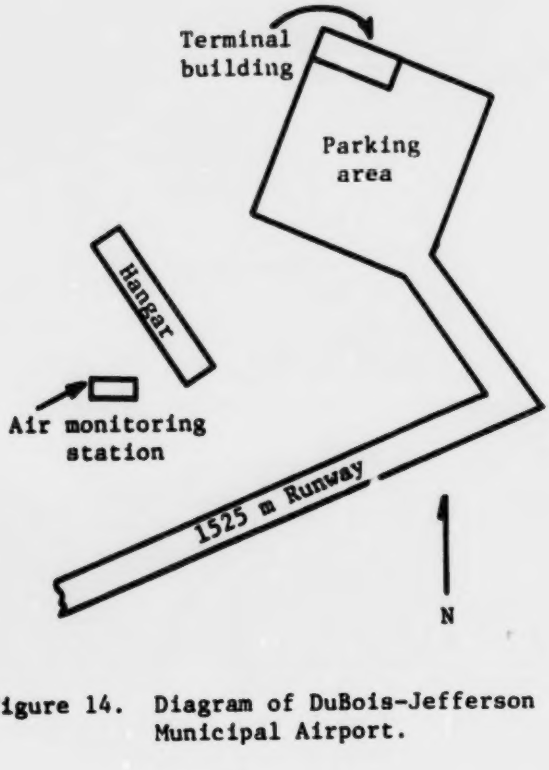

Terminal building
Parking area
Hangar
Air monitoring station
1525 m Runway
N

Figure 14. Diagram of DuBois-Jefferson Municipal Airport.

3.1.2.4 DuBois, Pennsylvania (DuBois-Jefferson Municipal Airport)

The DuBois, Pennsylvania, station was located at the DuBois-Jefferson Municipal Airport 13 kilometers northwest of DuBois, Pennsylvania. The site is 554 meters above mean sea level and is well ventilated. An aerial view of the site with respect to the surrounding terrain is shown in figure 14. Instrumentation and associated equipment to measure O_3 and NO_2 concentrations were housed in a 2.4-by-4.6-meter construction trailer, similar to the trailer shown in figure 12 and parked approximately 183 meters away from, but parallel to the runway. An air-sampling inlet system identical to that used at the previously mentioned stations was used to bring sample air to each analyzer. The DuBois station was not a manned station, but was checked daily by an employee of the airport.

3.1.2.5 McHenry, Maryland (Garrett County Airport)

The McHenry, Maryland, station was located at the Garrett County Airport, approximately 884 meters above mean sea level. The airport complex consists of 762-meter paved landing strip, an apron, hangars, and a terminal building. The airport is mainly used by small, private aircraft.

Figure 15 is a diagram of the airport which shows the location of the air-monitoring station. An exterior view of the station is shown in figure 16. Ozone and NO_2 concentrations were measured at this site. The air quality analyzers, strip-chart recorders, and data-acquisition system were located in a small workroom at the east end of the hangar. The interior environment of the station was controlled by an 18,000 Btu heating/cooling system. The ambient air inlet system and operation of the analyzers at this unmanned station were identical to those at the DuBois station.

3.1.3 Air Quality Measurements

3.1.3.1 Instrumentation

Ambient ozone concentrations were measured at all stations (i.e., rural, urban) using the Bendix Model 8002 chemiluminescent ozone analyzer or equivalent. The principle of operation of this instrument is based on the gas-phase chemiluminescent reaction between ethylene and ozone. The reliability, stability, specificity, and precision of the ozone measurements by this technique have been demonstrated and adequately described in the literature[6/].

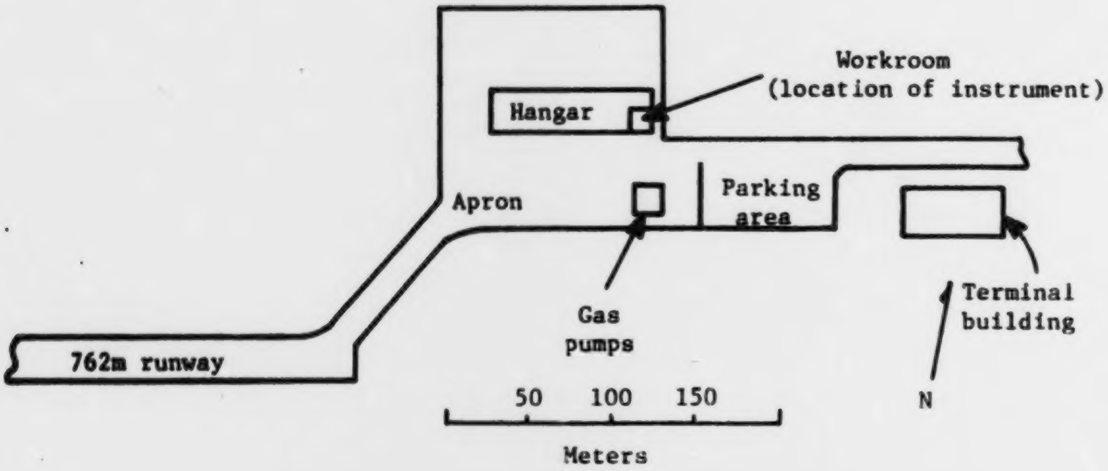

Workroom
(location of instrument)
Hangar
Apron
Parking
area
Gas
pumps
Terminal
building
762m runway
50
100
150
Meters
N

Figure 15. Diagram of Garrett County Airport.

Figure 16. Exterior view of McHenry, Maryland, (Garrett County Airport) station.

Nitrogen dioxide concentrations were measured at all stations using the Bendix Model 8101-B NO-NO_x-NO_2 analyzer. The principle of operation of this instrument is based on the gas-phase chemiluminescent reaction between NO and O_3. The measurement of NO_2 concentration by this instrument requires that NO_2 be reduced to NO prior to the reaction with O_3. The sum of the NO measurement plus that produced by reducing NO_2 to NO is the nitrogen oxide (NO_x) concentration. Subtraction of the previous NO measurement from the NO_x measurement gives the NO_2 concentration.

Nonmethane hydrocarbon (NMHC) concentrations were measured at three stations (i.e., Wilmington, Wooster, McConnelsville) using the Beckman 6800 air quality chromatograph. The Beckman 6800 air quality chromatograph utilizes an automatic gas chromatographic-flame ionization detector (GC-FID) to measure THC and CH_4 in ambient air. The NMHC concentration of the ambient sample is computed by subtraction of CH_4 from the THC measurement.

Detailed hydrocarbon analyses of grab samples collected during aircraft flights and at manned ground stations in Ohio were obtained by the Chemistry and Physics Laboratory of the Environmental Protection Agency using a Perkin-Elmer Model 900 chromatograph system. The system consisted of two Perkin-Elmer Model 900 chromatographs with a PEP-1 data-reduction system. Three columns were employed for the analysis of selected hydrocarbon fractions: 1) a 2.4-m x 0.15 cm i.d. silica gel at 30°C (C_2-C_5 aliphatics), 2) a 91.4-m x 0.15 cm i.d. dibutylmaleate open tubular column at 0°C (C_4-C_8 aliphatics), and 3) a 91.4-m x 0.15 cm i.d. open tubular column coated with m-bis-m-phenoxyphenoxy benzene at 70°C (C_6-C_{10} aromatics). The analytical and sampling techniques system employed here has been well documented in the literature.[7/]

3.1.3.2 Instrument Calibration and Maintenance

Dynamic calibration techniques were used to calibrate each analyzer at 2-week intervals during the 75-day period of field operations and are outlined in table 2. Data obtained from the calibrations were used to provide updated transfer equations for converting voltage outputs to pollutant concentrations in physical units ($\mu g/m^3$).

Table 2. Calibration techniques

Pollutant	Calibration technique
Ozone	Ultraviolet ozone generator referenced to the neutral-buffered potassium iodide method (Federal Reference Method)
Nitric oxide/nitrogen dioxide	Gas phase titration technique
Hydrocarbons (THC, CH_4)	Standard calibration gas certified as to CH_4 and THC content
Selected hydrocarbons	Mixtures prepared from pure hydrocarbons

Brief descriptions of the calibration techniques cited in table 2 follow:

1. Ozone--Ultraviolet ozone generator referenced to the neutral-buffered potassium iodide (KI) method.

Dynamic calibration of the ozone analyzers was accomplished by use of an ultraviolet ozone generator. The ozone source consists of a shielded 20.3-cm mercury vapor lamp which irradiates a 1.6-cm quartz tube through which clean (compressed) air flows at 5 ℓ/min. Variable ozone concentrations over the measurement range can be generated by variable shielding of the lamp envelope. Although the ultraviolet ozone generator had been shown to be quite stable and reproducible, the neutral buffered KI method was used as the reference method.

2. Nitric oxide/nitrogen dioxide--Gas phase titration technique.

The gas phase titration technique developed by Hodgeson and associates at the Environmental Protection Agency was used for dynamic calibration of the chemiluminescent $NO\text{-}NO_x\text{-}NO_2$ analyzers. The technique is based on the application of the rapid gas phase reaction between nitric oxide and ozone to produce a stoichiometric quantity of nitrogen dioxide. Nitric oxide (61 mg/m^3) in nitrogen (contained in pressurized cylinders) is diluted with zero air to provide NO concentrations in the range 20 to 940 $\mu g/m^3$ and used to calibrate the NO and NO_x channels. Nitrogen dioxide concentrations are produced by quantitative reaction of NO with ozone. Primary calibration of the concentration of NO in nitrogen was achieved by titration of an NO concentration of 1.2 mg/m^3 with successive concentrations of ozone (0 to 1.6 mg/m^3) generated by an ozone generator referenced to the neutral-buffered KI method. The NO concentration of each cylinder was determined prior to going to the field, once per month in the field, and at the conclusion of the study.

3. Methane calibration gas.

Calibration of the hydrocarbon analyzers was accomplished using mixtures of stable gases prepared to exact concentrations in pressurized cylinders. Mixtures of methane in air purchased from Scott Research Laboratory with a certificate of analysis as to the methane and total hydrocarbon concentrations were used for all calibrations.

4. Selected hydrocarbons.

Hydrocarbon standards used to calibrate the Perkin-Elmer gas chromatograph were prepared at regular intervals using a dilution technique of pure compounds (i.e., 99.9 percent pure hydrocarbons) with hydrocarbon-free air. Concentration mixtures in the parts-per-billion to parts-per-million range were prepared using up to 50 compounds in the C_2 to C_{10} hydrocarbon range. Response factors were calculated by the computer system for subsequent use in the analysis routine. Comparison of the peak height, retention times, and area for hydrocarbons in standard mixtures were used to identify and quantify the various hydrocarbons collected in the grab samples.

A detailed discussion of the calibration methods and procedures utilized during this program is given in appendix A.

Routine maintenance of the automated instruments was performed by the operators at the three manned stations in Ohio. Maintenance of the instruments at the DuBois and McHenry stations took place during the regularly scheduled biweekly calibration trips. A complete record of operational status (i.e., operational, repairs, maintenance, calibration, inoperative, etc.) was maintained for each analyzer throughout the duration of the measurements program at each station. This information was necessary for quality control and for use in the data validation process.

When failures occurred, the instrument was brought back on line in the most expedient manner (i.e., by substitution and/or repair). Periods of failure and reasons are summarized in appendix B, "Performance Characteristics and Operational Summaries for Instruments."

3.1.4 Data Acquisition/Reduction

Ozone, NO_2, THC, and CH_4 concentration data at each station were recorded in analog form on strip-chart recorders and in digital form on magnetic tape recorders. The strip-chart recorders were used for backup data in case of failure of the magnetic tape unit and also as a real-time record for assessment of the operational status of each analyzer. Primary data storage was on magnetic tape.

Due to the unavailability of five identical data acquisition systems and to other time constraints, three different systems were used to record data at the five rural stations. Metrodata DL-630 data loggers were used at the McConnelsville and Wooster stations; Westinghouse Pulse-O-Matic recording systems were used at DuBois and McHenry; and a Hewlett-Packard 2015H data-acquisition system and HP-2100A computer were used at the Wilmington station. A brief description of each data-acquisition system is presented in the following paragraphs.

The Metrodata Model DL-630 data system used at Wooster and McConnelsville, Ohio, is a complete data-acquisition system capable of recording up to 40 channels of analog data plus a time code, station identification, and manual data entry on magnetic tape. Commands are locally selectable via front-panel, lighted push buttons. Channel selection allows the observation of the existing signal on any channel on the front panel, three-digit display in essentially real-time. The scan rate is 40 channels/second and data are recorded on magnetic tape at 5-minute intervals.

The Westinghouse Pulse-O-Matic magnetic tape data acquisition system used to record data at DuBois, Pennsylvania, and McHenry, Maryland, integrates the signal from the air quality analyzer for a 15-minute interval and provides a true 15-minute average. A battery backup unit is included in the recorder to preserve the time information on magnetic tape in the event of a power failure.

The Hewlett-Packard data system used at the Wilmington station consists basically of a digital magnetic tape data acquisition system and an HP-2100 computer. The signals from the respective analyzers are scanned at 5-minute intervals. These sampled voltages are digitized and recorded on the magnetic tape in computer-compatible format; in addition, the scanned data are introduced into the minicomputer where the appropriate transfer functions are applied to each of the analyzer signals and the resulting values in concentration units are printed out. Five-minute data are accumulated, and at the end of each hour a summary, which includes the 5-minute data plus the hourly average, is printed out for immediate use.

Field data recorded on magnetic tape from the Metrodata, Westinghouse, and Hewlett-Packard data-acquisition systems were returned to Research Triangle Institute for processing on a weekly and/or biweekly basis. The data manipulation required to recover the data stored on a magnetic tape consisted of two phases:

1. Translation of the tape to a form compatible with available data-processing equipment, and
2. Processing the data on a computer to obtain concentrations in $\mu g/m^3$.

The end result was a hard-copy printout, which was then available for inspection and validation. This printout consists of the date, station identification, hourly average of 5- or 15-minute readings, and 24-hour average concentrations in $\mu g/m^3$ for each pollutant.

In order to obtain a printout of data that contained all the information, certain supplementary data had to be supplied to the computer. These data included times when the instruments were inoperative or not functioning properly and linear best-fit equations relating the voltage output of the instrument to the concentration of the pollutant being measured. The times for instruments being inoperative came from operator logs, calibration log sheets, quality control charts, examination of preliminary computer runs, and strip charts. The equations were derived from data obtained during calibration--the known input gas concentrations and the resulting voltage output from the instrument. A regression analysis was performed on these points to obtain a best-fit equation characterizing the instrument's response. The printout produced by the computer then contained the data in $\mu g/m^3$. If data were absent or invalid, the number 99999.9 and a code letter were inserted to indicate the reason for loss of data. A sample page of printout is shown in figure 17.

```
                       RTI EASTERN REGIONAL OZONE STUDY

                              WILMINGTON, OHIO

                  UG/M3 CONCENTRATION          AUG  22,1974

TIME(EDT) BX 03  S  RTI 03 S  BX NO  S  BX NO2 S BK THC  S BK CH4  S BK CO  S
1200 1215  148.      162.      3.        4.     1104.     1021.     215.
1215 1230  149.      161.      4.        5.     1107.     1039.     190.
1230 1245  145.      159.      4.        5.     1068.     1030.     216.
1245 1300  150.      165.      4.        5.     1057.     1027.     184.
1300 1315  156.      170.      3.        3.     1048.     1031.     196.
1315 1330  157.      170.      3.        4.     1297.     1033.     234.
1330 1345  163.      173.      3.        6.     1050.     1027.     212.
1345 1400  164.      180.      3.        5.     1043.     1024.     205.
1400 1415  174.      183.      4.        3.     1052.     1030.     199.
1415 1430  174.      183.      3.        5.     1063.     1028.     156.
1430 1445  169.      189.      4.        6.     1053.     1040.     212.
1445 1500  181.      188.      3.        7.     1052.     1038.     210.
1500 1515  185.      198.      3.        6.     1040.     1032.     234.
1515 1530  187.      195.      4.        4.     1050.     1023.     227.
1530 1545  186.      197.      4.        5.     1044.     1013.     199.
1545 1600  188.      188.      3.        5.     1058.     1014.     181.
1600 1615  185.      195.      3.        4.     1053.     1023.     196.
1615 1630  184.      198.      2.        5.     1048.     1012.     194.
1630 1645  176.      195.      2.        3.     1046.     1013.     196.
1645 1700  177.      185.      3.        5.     1037.     1005.     168.
1700 1715  178.      184.      2.        4.     1076.     1014.     174.
1715 1730  176.      188.      3.        2.     1031.     1009.     188.
1730 1745  185.      189.      2.        3.     1049.     1016.     207.
1745 1800  190.      197.      2.        5.     1033.     1019.     209.
```

Figure 17. Typical data printout.

3.1.5 Data Validation and Quality Control

In order to achieve and maintain a high level of confidence in air quality data, it is essential to monitor routinely critical instrument parameters and to maintain appropriate records. Quality control was initiated for the summer oxidant study by verification of calibration procedures, standards, and operating procedures, performing dynamic calibrations at specified intervals; maintaining adequate records; and thoroughly training operators.

Calibration data, as well as daily zero and span information when available, were examined for excessive zero and span drift. If zero drift exceeded ± 1 percent of full scale per 24-hour period, the data of the preceding 24-hour period were of questionable validity. Span drift was determined from multipoint calibration data every 2 weeks. Span drift exceeding ± 3 percent per 2 weeks was usually associated with instrument malfunction, and the data were deleted.

To verify data-recorder accuracy, a constant voltage data input standard was recorded every 5 minutes (or 15 minutes) in conjunction with the air quality data. It was not necessary to invalidate any ambient air quality data resulting from analog-to-digital conversion errors.

At the completion of each computer program set, the processed data were compared with strip-chart data for randomly selected periods. A typical check included comparison of computer-processed data and strip-chart data for six selected 1-hour averages per day. The recorded data on strip charts were also edited for signs of equipment malfunctions, excessive pollutant levels, or unusual diurnal patterns.

3.2 Aircraft Measurement Program

3.2.1 Aircraft Flight Protocol

The two basic flight patterns flown during the field measurement program were described in section 2.1.2, "Airborne Measurements." In addition to these basic patterns, vertical profile flights and one eastern wide area flight were flown. An RTI meteorologist at the base station provided the RTI field manager with all meteorological information necessary to make decisions regarding when to fly and the type of aircraft mission to be flown. His secondary duties included preflight planning, accompanying the actual mission as an airborne observer, and finally assimilating and summarizing the mission data into a useful format.

To perform the primary duty, the field meteorologist kept abreast of the general synoptic weather situation through information provided by local news media, supplementing this with real-time surface data obtained from the Operation Section of Overseas National Airways located at Wilmington Industrial Air Park. The primary criterion for a mission was the condition of relatively clear skies at or below the flight level. When such conditions were forecast for the following day, the RTI field manager and the EPA flight crew were alerted. At 0845 the morning of the projected mission, the meteorologist telephoned the National Weather Service Upper Air Station at Dayton and obtained data for the lower 500 millibars from their morning radiosonde flight. From the Dayton sounding, the meteorologist computed the stability and forecast the depth of thermal mixing and the heights of cloud layers that might form later in the day. Using this information and the vertical wind profile, the decision was then made to fly either a double box or a square wave, providing all other flight conditions such as adequate VFR visibility and no severe weather forecast for the mission area still prevailed. The sounding was also used to select a flight altitude in the mixing layer but below any clouds that might form. In the case of the square wave, wind direction at flight altitude determined the orientation of the pattern.

Vertical ascents were occasionally flown when the meteorologist noted some interesting features in the temperature profile, such as a subsidence inversion. The long eastern wide area flight had only one meteorological criterion, that of stagnant high pressure. Flight altitude was a function of topography, and the pattern was determined by navigational criteria.

3.2.2 Aircraft System Description

Instrumentation for the measurement of ozone, oxides of nitrogen, and temperature and equipment for the collection of grab samples were installed aboard a C-45H aircraft, provided by the National Environmental Research Center at Las Vegas, Nevada. The C-45 aircraft (fig. 18) with a full load

Figure 18. Photograph of aircraft.

of fuel has a capacity for 340 kg of instrumentation and a crew of four--pilot, copilot, meteorological observer, and instrument operator. Under these conditions, the C-45 has an average cruising speed of 130 knots, a climb rate of 152 m/min, and a flight range of approximately 5 hours. Navigation equipment includes two VOR units with DME, and ADF, and a flux-gate compass.

The air intake system used on the C-45 is illustrated in figure 19 and consisted of a 5-cm i.d. aluminum probe permanently mounted on the underside of the aircraft nose approximately 1 meter forward of any point on the plane. The probe was lined with 2.5-cm i.d. Teflon tubing to minimize reaction of air pollutants with the manifold wall.

The other end of the Teflon tube extended inside the aircraft cabin. Two 0.635-cm i.d. Teflon tubes and a temperature-sensing thermister were inserted well into the 2.5-cm i.d. Teflon tube. One of the 0.635-cm i.d. Teflon lines was connected to a glass sample manifold from which the O_3 and NO_x analyzers sampled. Ram pressure created by air rushing through

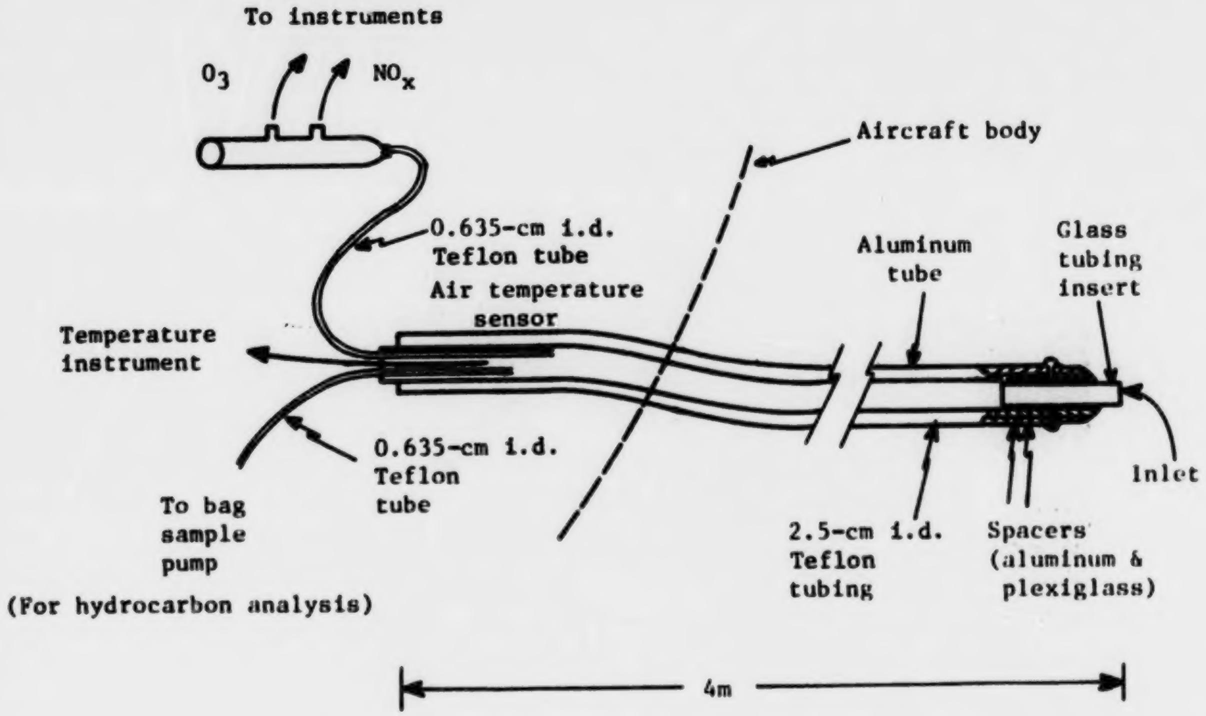

To instruments
O_3
NO_x
Aircraft body
0.635-cm i.d.
Teflon tube
Air temperature
sensor
Temperature
instrument
Aluminum
tube
Glass
tubing
insert
0.635-cm i.d.
Teflon
tube
Inlet
To bag
sample
pump
(For hydrocarbon analysis)
2.5-cm i.d.
Teflon
tubing
Spacers
(aluminum &
plexiglass)
4m

Figure 19. Air-sampling probe used on C-45 aircraft.

the 2.5-cm i.d. tube forced a steady flow of sample air into the cabin manifold. The pressure in the manifold was essentially that of the unpressurized aircraft cabin, which prevented the pressurization of the instrument sample inlets. The other 0.635-cm i.d. Teflon line was connected to a stainless steel diaphragm pump used to fill sample bags. The air sample inlet system was designed for a minimum of sample contamination by emissions from the aircraft itself. Ram pressure caused an airflow through the Teflon tube providing sufficient flushing to keep gases within the aircraft cabin from diffusing into the tube and contaminating the air sample stream. Tests were conducted to insure that contamination from the interior of the aircraft was not getting into the sample manifold.

A block diagram of the instrumentation installed in the C-45 is shown in figure 20 and included an RTI solid-phase ozone analyzer, a Bendix

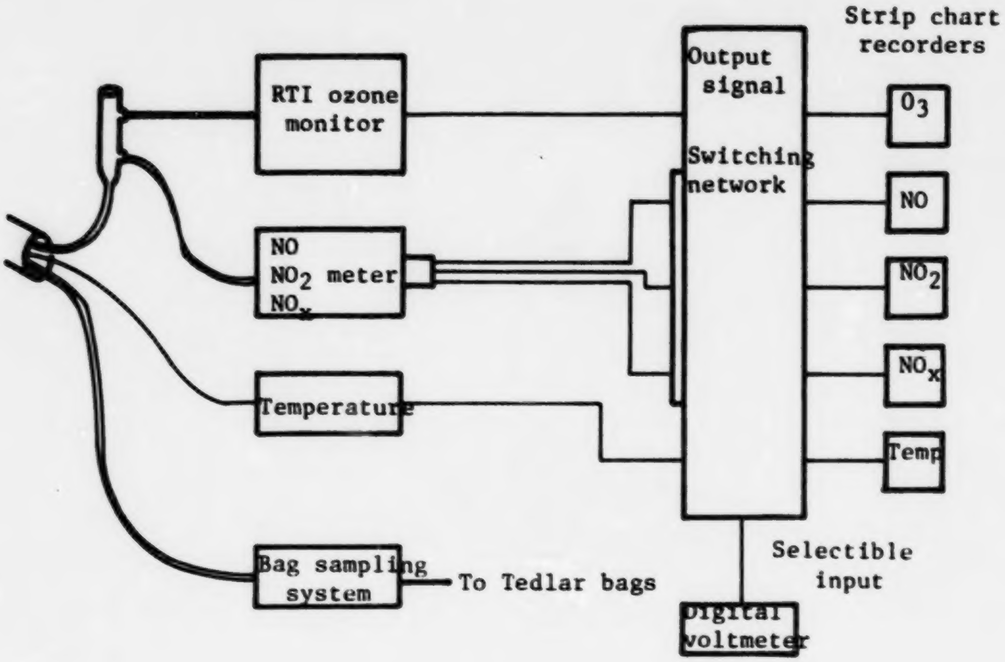

Strip chart recorders
RTI ozone monitor
Output signal
Switching network
O_3
NO
NO_2 meter
NO_x
NO
NO_2
NO_x
Temperature
Temp
Bag sampling system
To Tedlar bags
Selectible input
Digital voltmeter

Figure 20. Block diagram of aircraft instrumentation.

$NO-NO_2-NO_x$ analyzer, a Yellow Springs temperature sensor, an air sample pump, five strip-chart recorders, and a 2kW-Nova inverter. All instrumentation was shock mounted with Areoflex twisted steel rope shock mounts.

The ozone analyzer used in the aircraft is a solid-phase chemiluminescent instrument built by RTI. It is a self-contained instrument requiring no external pressurized gas supplies of any kind. The analyzer operates in a cyclic mode with a calibration signal response and a measure cycle response output once during each 2-minute cycle. The performance characteristics of the analyzer have been described in the literature.[6,8]

The Bendix 8101-B chemiluminescent analyzer was used in the aircraft to monitor oxides of nitrogen. Support equipment on board for this instrument included a compressed oxygen cylinder and a two-stage diaphragm vacuum pump. The sample inlet for the instrument was from the same manifold as the ozone analyzer.

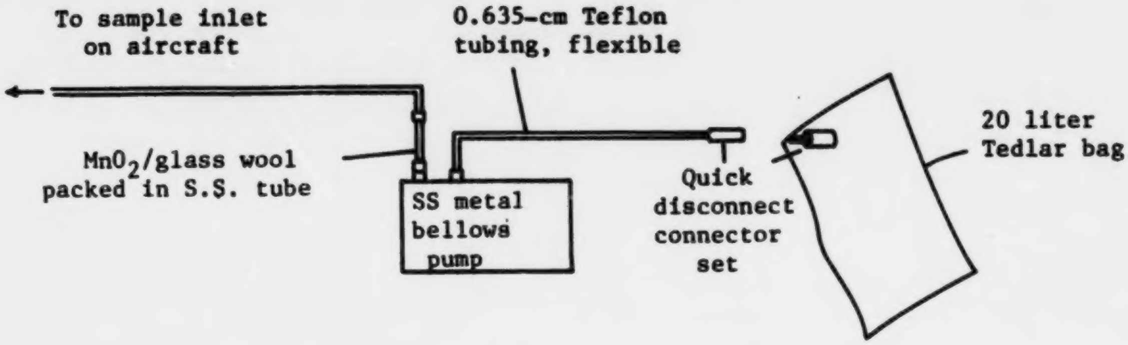

To sample inlet on aircraft
0.635-cm Teflon tubing, flexible
MnO_2/glass wool packed in S.S. tube
SS metal bellows pump
Quick disconnect connector set
20 liter Tedlar bag

Figure 21. Air sample bag-filling system.

The system used for collecting grab samples is shown in figure 21. The system consists of a stainless steel metal bellows pump with a manganese dioxide catalytic converter on the input to convert any ozone to oxygen. The output of the pump was connected to a 20-liter Tedlar bag with Teflon lines using stainless steel, quick-disconnect fittings.

Temperature changes in the sample airstream were monitored by the temperature section of a Yellow Springs Instrument Company Model 91 hygrometer. The temperature sensor, a small 0.635-cm diameter bead, was located just inside the sample inlet downstream from the points where the bag sample and ozone-oxides of nitrogen samples were drawn off.

The principal means of data acquisition aboard the aircraft were five strip-chart recorders, Hewlett Packard/Mosely Model 680 units, mounted in an instrument rack along with switching networks that allowed the monitoring of each of the inputs on a digital voltmeter or the application of a zero voltage to the recorders for a zero adjustment without disconnecting any cables.

The power for each of the instruments was supplied by a 2-kW Nova inverter powered by the aircraft 28-volt d.c. electrical system. The inverter was a well-regulated unit with current limiting for overload failure protection.

3.2.3 System Operation

Procedures for the operation of the aircraft instruments were established and documented early in the program so that data could be taken under uniform conditions in the event of a change of operators. Also, operating from predetermined procedures insured more consistent operation with the same operator.

Operational procedures for the aircraft are broken down into four categories: 1) preflight, 2) inflight, 3) routine calibration, and 4) ground operation. The procedures for each area are listed step-by-step in appendix E. The general objectives accomplished by the procedures are described in the following paragraphs.

1. Preflight.

Preflight checks were made in order to insure that all instruments were working and set to the proper range and mode of operation. Also, the strip-chart recorders were checked for operation. The manifold was checked to insure that the instruments were connected properly. These procedures were set to insure that valid data collection began as soon after takeoff as possible and that minimum data were missed due to instruments being improperly set.

2. Inflight.

The primary function of the instrument operator was to annotate the strip charts with time and to observe the instruments for symptoms of erratic or abnormal operation. The meteorological observer operated the bag sample apparatus and made pertinent observations of weather conditions and aircraft location.

3. Routine calibration.

Routine calibrations were conducted on each of the gas analyzers in the aircraft each day for which a flight was planned. Calibrations were conducted against the instruments in the van which were considered as "secondary field standards." The aircraft calibration was accomplished in two steps: 1) calibration of a portable calibration unit and 2) calibration of the analyzers using the portable calibration unit. The procedures involved are discussed in section 3.2.4.1.

4. Ground operation.

The instruments aboard the aircraft were operated continuously during the summer study. Immediately after landing and taxiing to the aircraft tie-down position, a 117-volt a.c. source was connected to the instrumentation before the aircraft engines were shut down. Prior to takeoff, at least one engine was started, bringing a generator into operation before ground power was disconnected from the aircraft instrumentation system. Since the aircraft sampling probe system was designed only for operation during flight, an alternative means was needed for supplying sample air to the instruments while on the ground. This was accomplished by connecting 0.635-cm Teflon lines to the instrument inlet. Each Teflon line extended through the cockpit window and was supported approximately 1 meter above the aircraft. Concentration values of nitrogen dioxide and ozone could then be read from the instruments in the aircraft and compared to those values being measured in the base station.

3.2.4 Instrument Calibration/Altitude Effects/Data Validation

3.2.4.1 Instrument Calibration

All gas analyzers were calibrated immediately before each flight. The gas analyzers in the RTI van were of the same type as those used in the aircraft and were considered secondary standards for the aircraft calibrations. Specifically, the output concentration of a portable calibration unit capable of generating O_3, NO, and NO_2 was determined by connecting it to the analyzers in the base station and observing their response. The portable unit was then carried to the aircraft and operated under the same conditions (flow rates, pressures, line voltage, etc.) as in the base station. The aircraft instruments were connected to the portable calibration unit, and either the span was adjusted to its proper setting (in the case of the Bendix $NO-NO_2-NO_x$ analyzer), or the internal calibration level was determined (in the case of the RTI ozone monitor). Zero determinations for the NO_2 instrument were carried out by connecting a clean-up system to the sample input of the analyzer. No zero adjustment was necessary on the ozone analyzer by virtue of the way the output is computed. The temperature-measuring instrument aboard the aircraft did not require frequent calibration due to its inherent stability. It was calibrated at the beginning and end of the program and twice between. The calibration consisted of a two-point calibration, one at 0°C determined by an ice bath and one at ambient temperature as measured by a lab-type mercury thermometer.

3.2.4.2 Altitude Effects on Instrumentation

The environmental test chamber facility at NERC, Las Vegas, was used to determine the effects of change in altitude on instrument responses prior to their use in the aircraft measurement program. This facility consisted of a sealable chamber approximately 71 cm x 81 cm x 152 cm high. Temperature, dew point, and pressure could be set by control units external to the chamber and could be varied during the test.

A series of tests was run on three instruments, the RTI ozone monitor, a Bendix ozone analyzer, and a Bendix NO-NO_2-NO_x analyzer. Each instrument was placed in the chamber and calibrated. Then a constant concentration of the gas being measured by the instrument was input to the instrument through a port in the side of the chamber. The calibration gas was input to the instrument through a glass manifold open to the inside of the chamber to insure that the pressure on the sample inlet was the same as the chamber pressure. The chamber then was depressurized in increments to the pressure equivalent of 3,658-meter altitude (and beyond in some tests) while the response of the instrument was being monitored on two strip-chart recorders. Results of multiple runs of this test were processed to produce a curve for each instrument. From this curve the percentage decline in instrument response at a given altitude was determined. Curves for the two instruments used in the aircraft are included in figures 22 and 23. A detailed description of the test is included in appendix D.

In addition to the tests run in the chamber, tests of instrument behavior were performed on the ozone instrument while airborne. A standard calibration system using an ultraviolet ozone source and rotameter was used aboard the aircraft with a modification on the output. A restriction was placed on the output, along with a vent controlled by a valve (see fig. 24). By closing the valve, the calibration system could be pressurized.

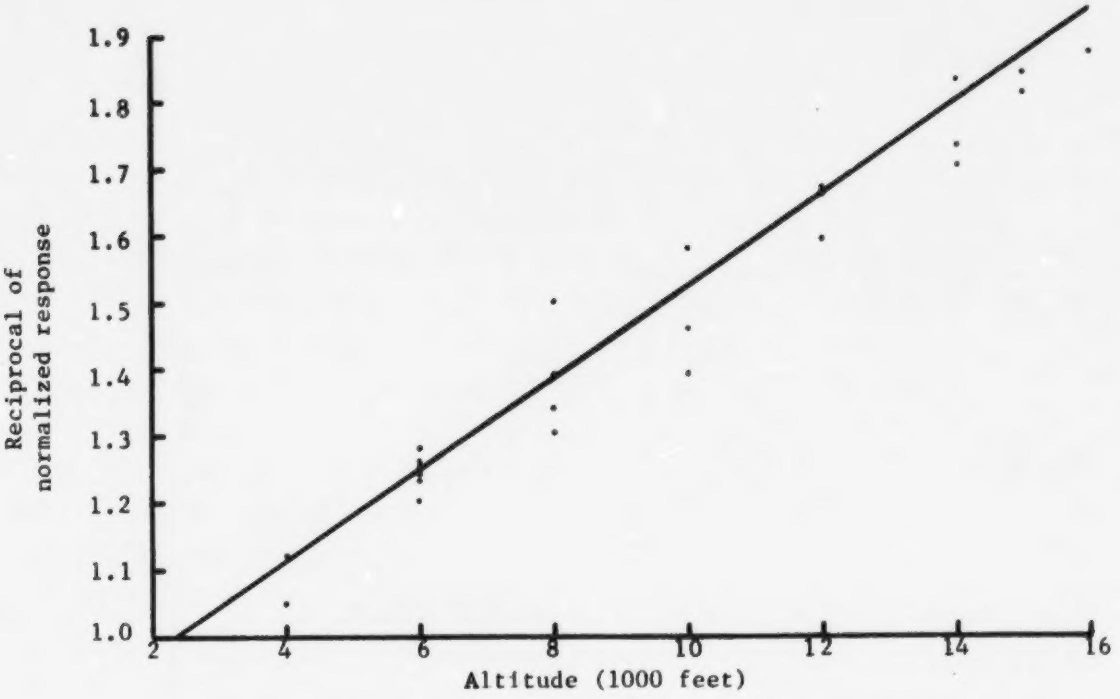


Figure 22. Compensation factor for adjustment of Bendix NO-NO_2-NO_x analyzer data for effects of altitude.

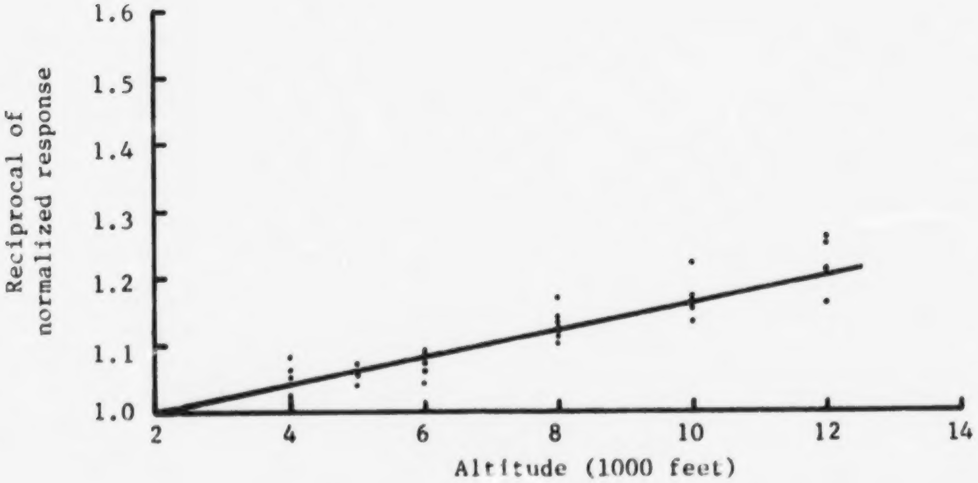


Figure 23. Compensation factor for adjustment of RTI ozone analyzer data for effects of altitude.

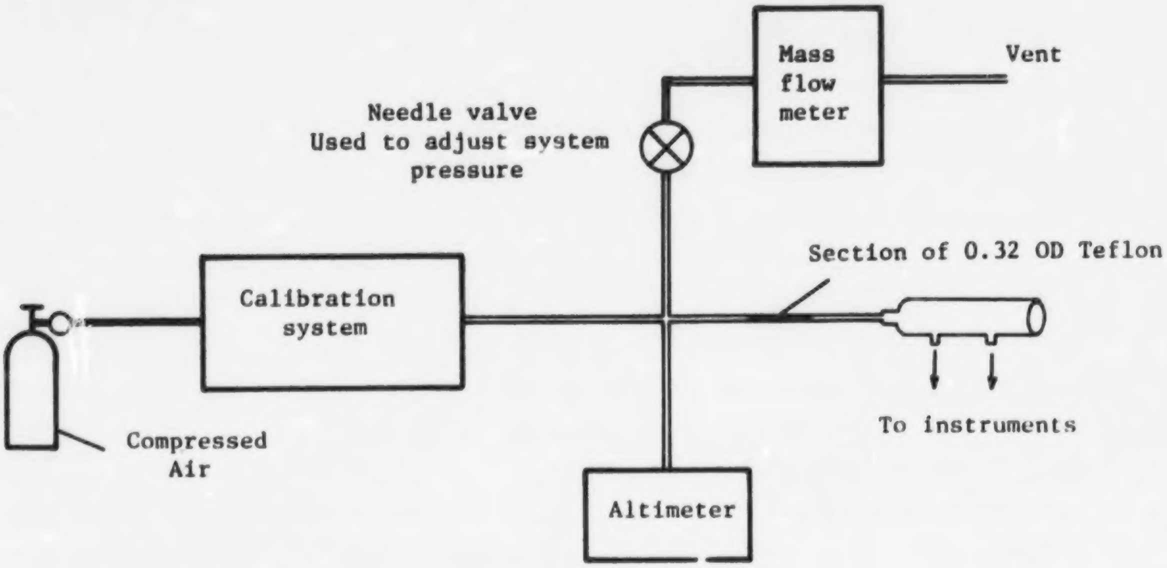

Mass flow meter
Vent
Needle valve Used to adjust system pressure
Section of 0.32 OD Teflon
Calibration system
To instruments
Compressed Air
Altimeter

Figure 24. System used to calibrate analyzers while airborne.

An altimeter was connected to the system so that the pressure could be adjusted to the same level as it was on the ground. The flow out the vent was monitored and the length of the 0.32-cm Teflon restriction adjusted so that the flow out the vent did not exceed 1 ℓ/min (at standard conditions). This insured that sufficient calibration gas flowed through the manifold to keep it flushed and not contaminated with cabin air.

Proper operation of the instruments was verified at the different altitudes by measuring flow rate in flight. Sample flow rates were monitored for the instruments during the tests on the aircraft at the various altitudes. During routine flights, sample flow rates were checked periodically to insure that the operating conditions were unchanged. This insured that the results obtained during the altitude tests were still valid (including the correction curves).

The results of these inflight calibration and operational verification tests were in agreement with the tests run in the fixed chamber. Repeatedly it was shown that the response of the instrument declined linearly with ambient pressure.

3.2.4.3 Data Validation

Various steps were taken to insure the validity of the data other than those which were a part of the quality assurance program. These included: 1) low altitude passes above the base station with all instrumentation in operation, 2) comparison of readings in the aircraft while on the ground to those in the adjacent base station, 3) airborne comparison of readings in the EPA aircraft with readings in another aircraft independently instrumented and operated, and 4) hydrocarbon air sample contamination tests. Data were also obtained during the program to demonstrate the comparability of the RTI solid phase and Bendix gas phase chemiluminescent ozone analyzers.

Fly-by Comparisons

Fly-bys were conducted by flying the aircraft over Wilmington Industrial Air Park at an altitude between 15 and 30 meters above the terrain. Generally, the aircraft approached the field from the end opposite the base station (approach from the northeast) and flew over the taxiway parallel to the runway. Flying in this manner, the aircraft could safely achieve a lower altitude and hold it longer than flying from another direction over grass or wooded terrain. The time for the aircraft to fly from the end of the runway to the base station took approximately 30 seconds, which gave the instrument some time to stabilize before a reading was taken.

A plot of the results is included in figure 25. Here the readings taken from the airborne RTI instrument are plotted on the ordinate against the fixed base station 5-minute instantaneous sample readings taken closest in time plotted on the abscissa. Perfect agreement between the two instruments would be indicated by a plot in which all points fell on a line passing through the origin and inclined at an angle of 45°. The departure of the instrument behavior from this ideal is not unexpected. During the early hours of the day at a time when many of these passes were made, a homogeneous concentration of ozone due to mixing had not been achieved. This was borne out by observing the strip-chart trace in the aircraft during the measure cycle. It was frequently quite erratic, indicating variations in the concentration of ozone at different points surrounding the base station.

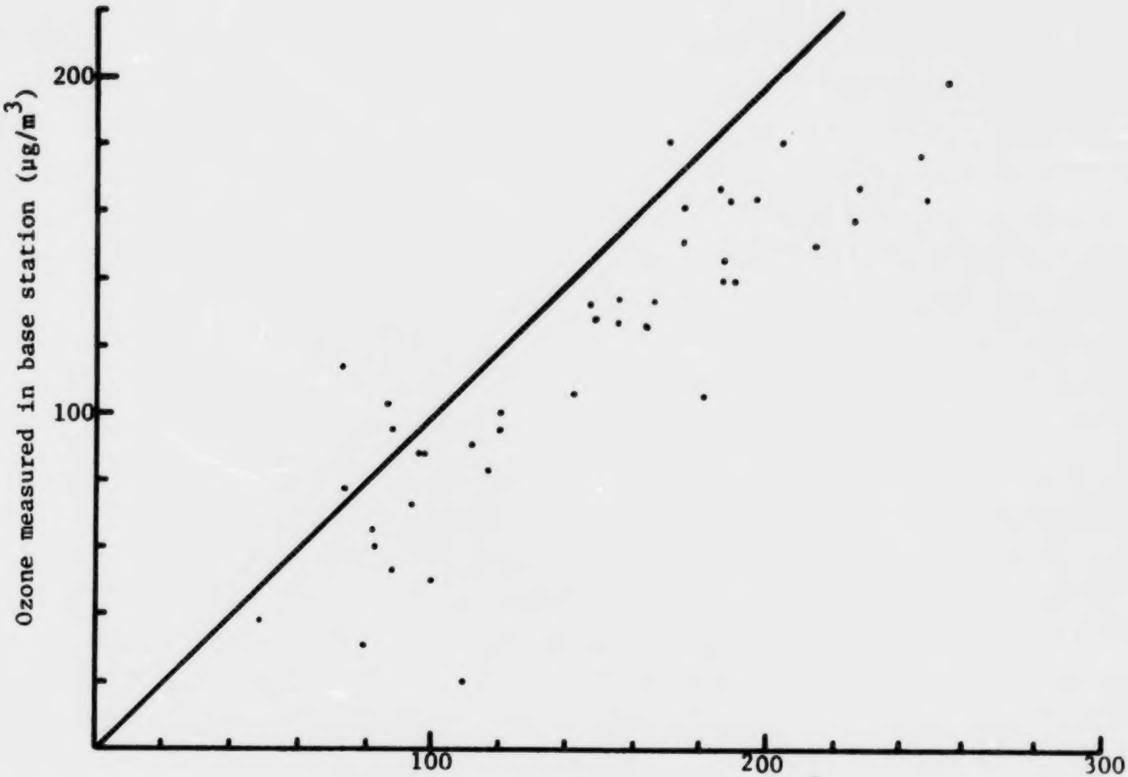


Figure 25. Aircraft fly-by data.

Ground Comparison Tests

Ground comparison tests were also used to check the aircraft measurement systems. These tests consisted of comparisons between the base station and aircraft instrumentation, while the aircraft was parked adjacent to the base station. The sampling ports for the aircraft and base station were located approximately 20 meters apart, at a height of 4 and 7 meters, respectively, above the ground. Figure 26 shows a plot of the aircraft and base station ozone concentration measurements during a selected time interval.

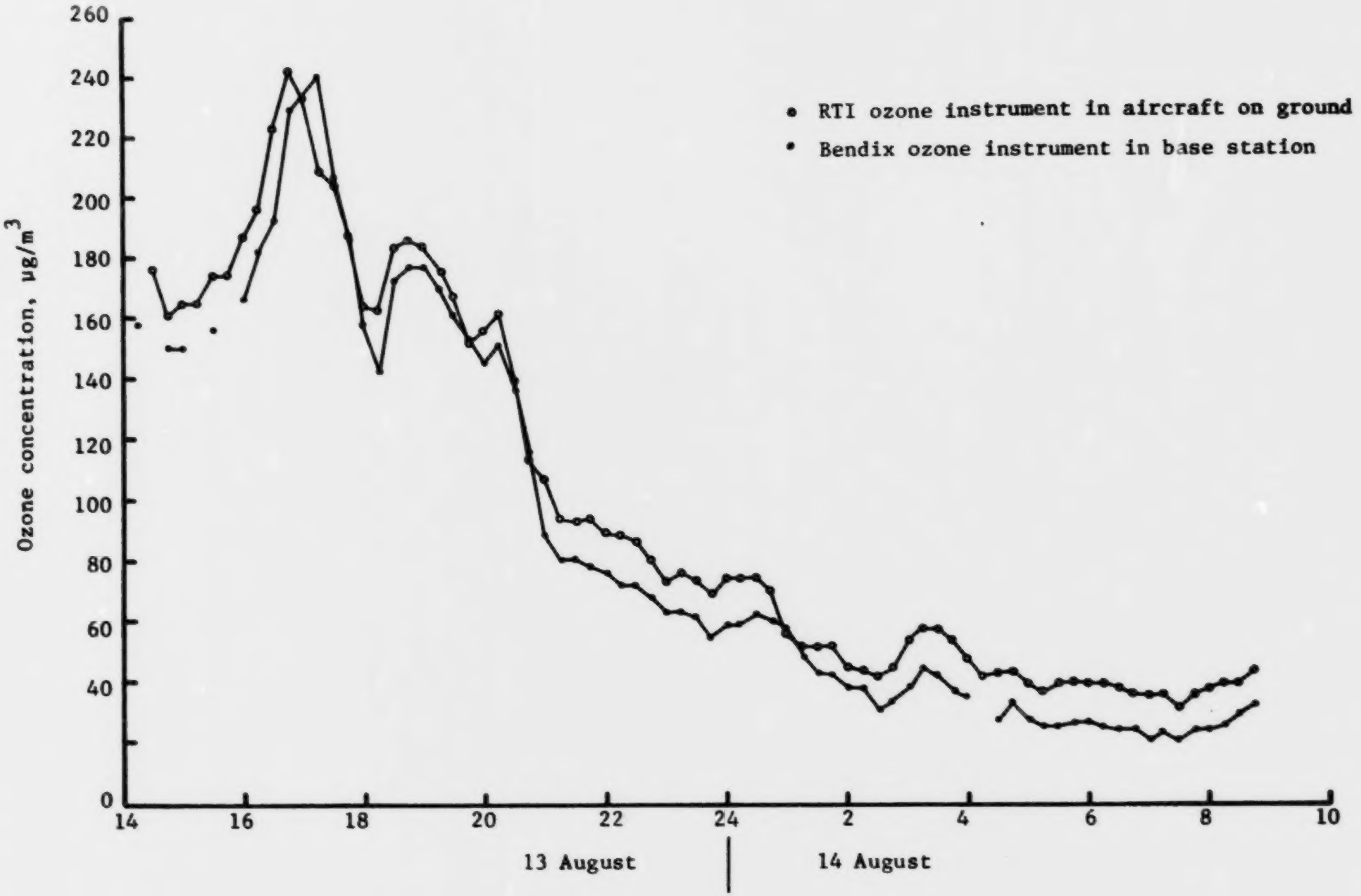


Figure 26. Plot of data from ozone instrument in aircraft while on ground and data from base station instrument.

Battelle Comparison Flight

A third means of insuring data validity was to determine the comparability between two similar aircraft measurements systems operating in the same environment. This test was conducted in conjunction with Battelle Memorial Research Institute. Battelle operated a Cessna 173 aircraft outfitted with a REM gas phase chemiluminescent ozone analyzer and ram-pressure bag-filling system. Due to the differences in cruising speed of the two aircraft, a formation flight could not be flown. The triangular pattern shown in figure 27 was flown twice by both aircraft with the EPA C-45 aircraft preceding the Battelle Cessna aircraft. A plot of comparable ozone data obtained during this flight is presented in figure 28. Ozone concentrations are plotted versus location along the flight path; consequently, there was a time difference between data obtained at the same point. The time difference varied with position on the flight plan.

The plot shows good agreement between the RTI instrument and the REM instrument over the duration of the flight path, the differences being typically less than 10 percent.

Hydrocarbon Sample Contamination Test

Another system test was conducted to verify the integrity of the sample inlet system. On the first flight, the gas chromatographic analysis of the bag samples indicated a high concentration of gasoline vapors. The logical deduction was that air from the interior of the aircraft was being drawn into the sample along with the ambient air. The sample inlet was modified to produce the system described and illustrated earlier (fig. 19). During a planned test flight, the contents of a lecture bottle of a known hydrocarbon were released continuously in the cabin during the collection of a bag sample. This bag was analyzed and the concentration of the known hydrocarbon observed and compared to ambient concentrations measured earlier during the flight. The test indicated that no detectable amount of cabin air containing the high concentration of the released hydrocarbon was evident in the bag sample. Since the sample inlet for the hydrocarbon bag sample was approximately 15-cm downstream from the ozone-oxides of nitrogen sample inlet, it was assumed that the ozone-oxides of nitrogen sample was uncontaminated as well.

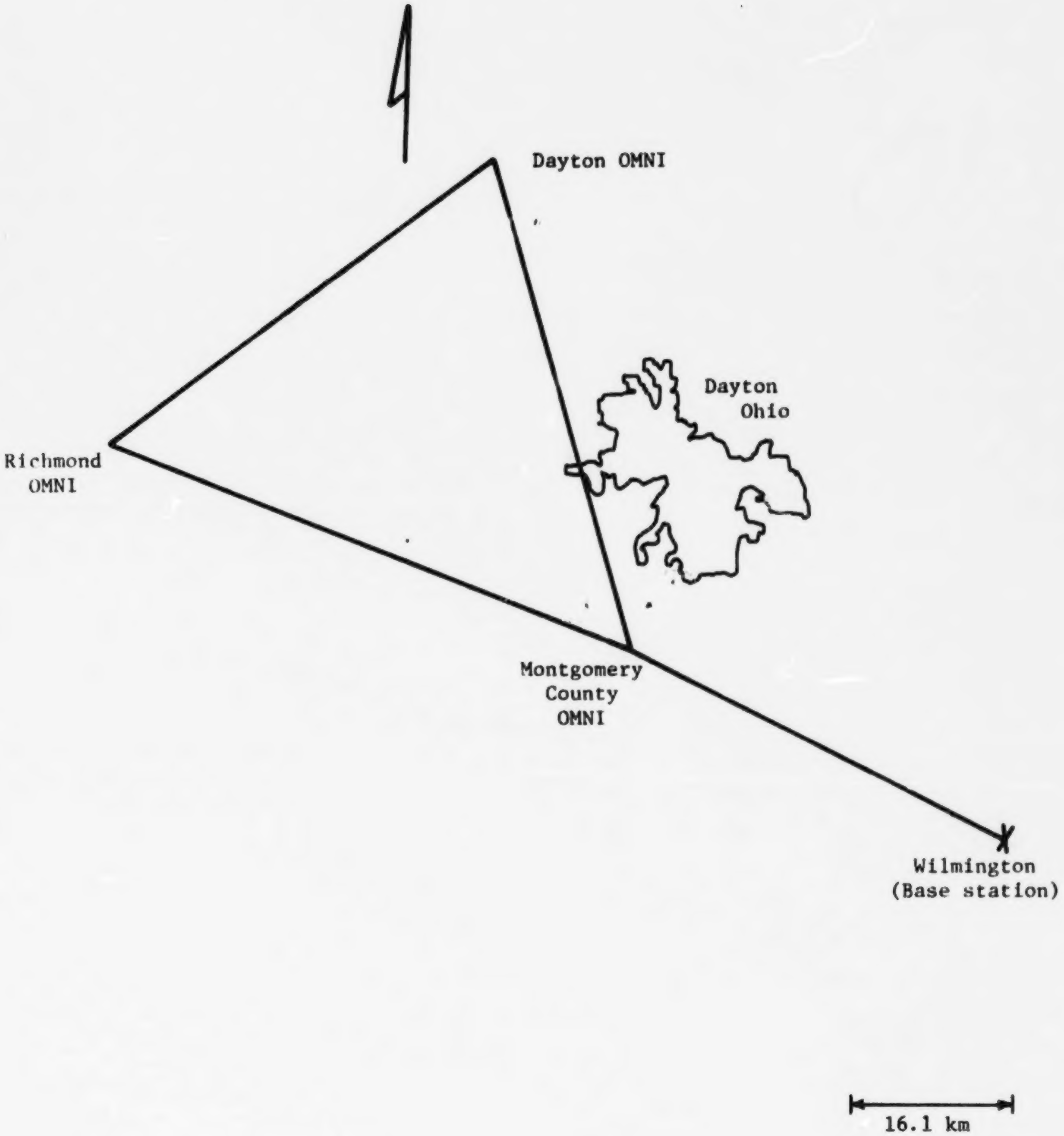

Dayton OMNI
Dayton
Ohio
Richmond
OMNI
Montgomery
County
OMNI
Wilmington
(Base station)
16.1 km

Figure 27. Battelle comparison flight pattern.

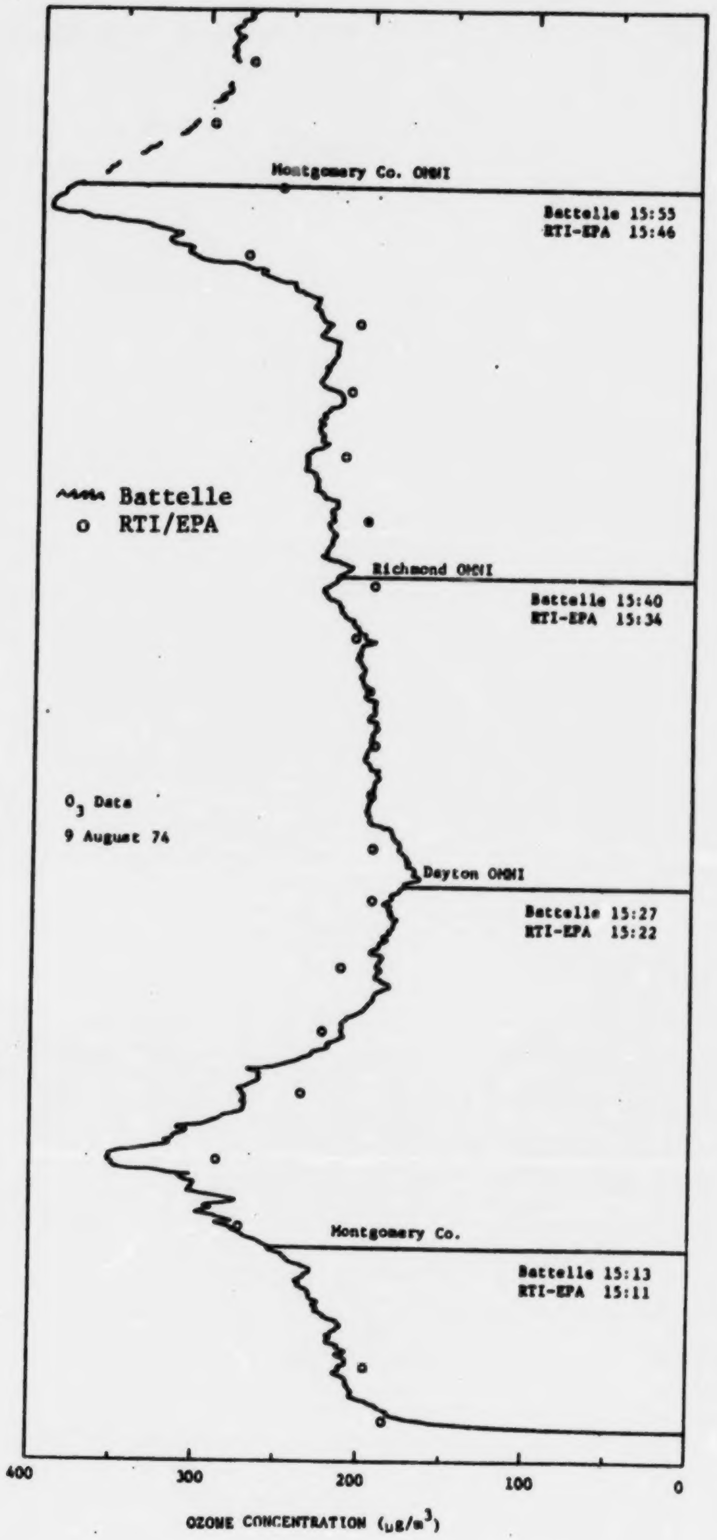


Figure 28a. Data from RTI/Battelle comparison flight.

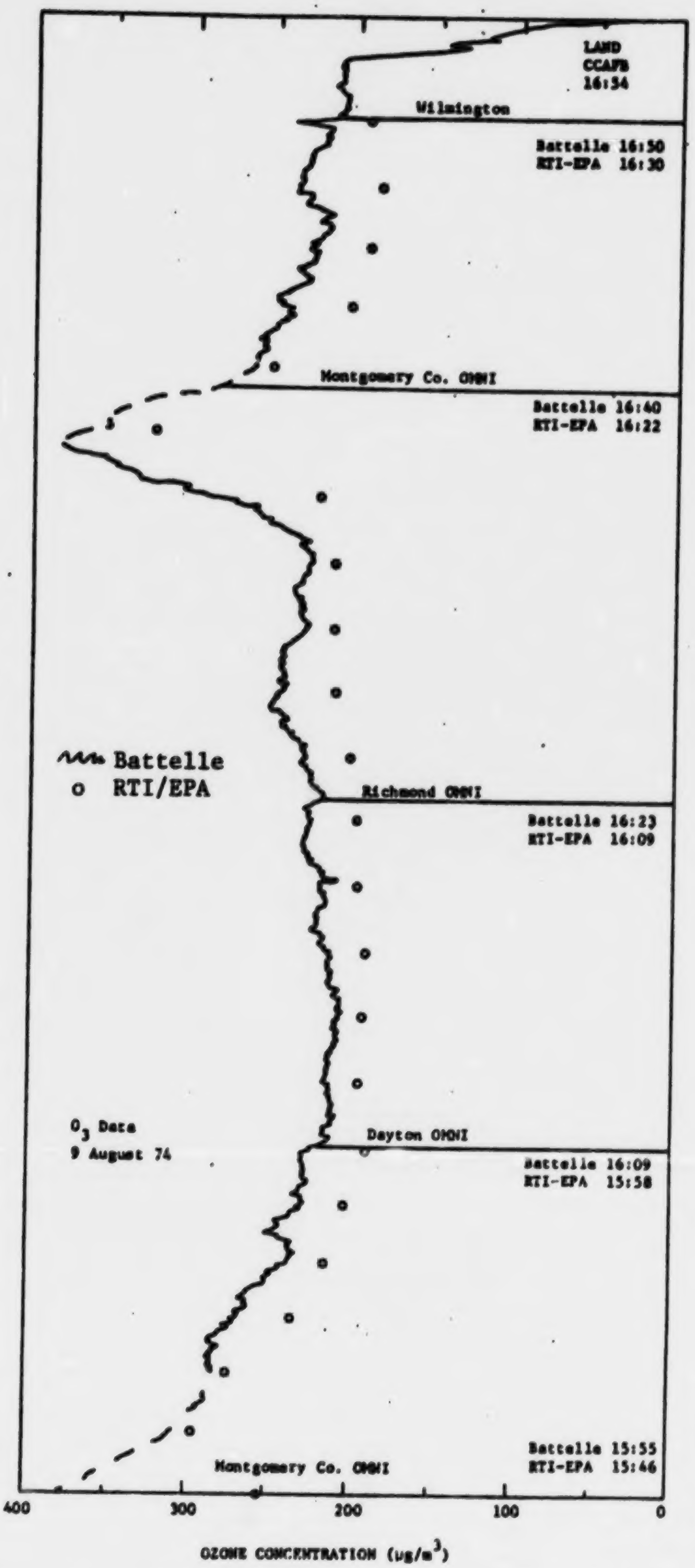


Figure 28b. Data from RTI/Battelle comparison flight.

A test for bag permeation was carried out by storing bags of zero air in the aircraft for long periods of time and reanalyzing them to see if any hydrocarbons permeated the bags; none was found.

3.2.4.4 Comparison of RTI Solid Phase and Bendix Gas Phase Ozone Analyzers

Tests were conducted to demonstrate the comparability of the RTI solid phase and Bendix gas phase chemiluminescent analyzers. These tests were conducted in the RTI Mobile Monitoring Laboratory with the two instruments located side by side. Both instruments were connected to the same sampling manifold through which ambient air was being aspirated. The output of each was sampled once every 5 minutes, 24 hours per day, and recorded on magnetic tape. The RTI ozone monitor used for this test had a set of three sample and hold modules and electrical analog subtraction and division circuitry, which carried out the function of comparing the measure signal level with the known internal calibrate. This removed the requirement for manually reducing the data as was done for the aircraft data (see section 3.2.5 for the procedure that was followed to accomplish this). Data recorded on the magnetic tape were processed by computer and printed out in concentration units (micrograms per cubic meter).

Tests were run on these instruments on two occasions: once in the spring of 1974 (April 17, 18, 19 and May 2, 3) and again in late summer 1974 (August 9-September 1), yielding ample data for comparative analysis.

A statistical analysis was performed on the data (spring and summer) to evaluate numerically the similarity of the readings. Results of this analysis are shown in table 3. The data were also graphed for the summer period and are presented in figure 29. The periods used for the statistical analysis are indicated on the graph. These data substantiate that the two instruments are comparable.

3.2.5 Data Acquisition/Reduction

The aircraft data-acquisition system used consisted of five Hewlett-Packard/Mosely 680 electric-writing, strip-chart recorders rack-mounted in a single unit. Also included in the unit was switching circuitry, which allowed the input of the recorders to be shorted without shorting each

Table 3. Results of statistical comparison of the RTI solid phase instrument versus Bendix gas phase instrument

Time Period Day	N*	Correlation	Means		Range		Std Dev		Mean Diff	Ratio of Means
			RTI	Ben	RTI	Ben	RTI	Ben	RTI - Ben	RTI / Ben
April 17	20	.96**	159	151	128-172	116-163	13	13	8	1.06
18	20	.99**	137	134	42-183	41-176	51	48	3	1.02
19	20	.96**	158	152	63-200	77-189	43	70	6	1.04
2	30	.99**	74	66	50-96	46-88	17	15	8	1.12
3	64	.99**	65	59	19-147	20-126	40	34	6	1.10
Aug. 7-9	547	.99***	86	81	24-152	9-154	30	34	5	1.05
14-16	632	.99***	94	95	20-161	19-177	35	43	-1	0.99
22-24	849	.98***	122	120	26-356	22-229	50	52	2	1.01
28-30	617	.97***	64	62	38-117	32-112	14	14	2	1.03

*Number of data points included in comparison.

**Based on hourly averages.

***Based on 5 minute values.

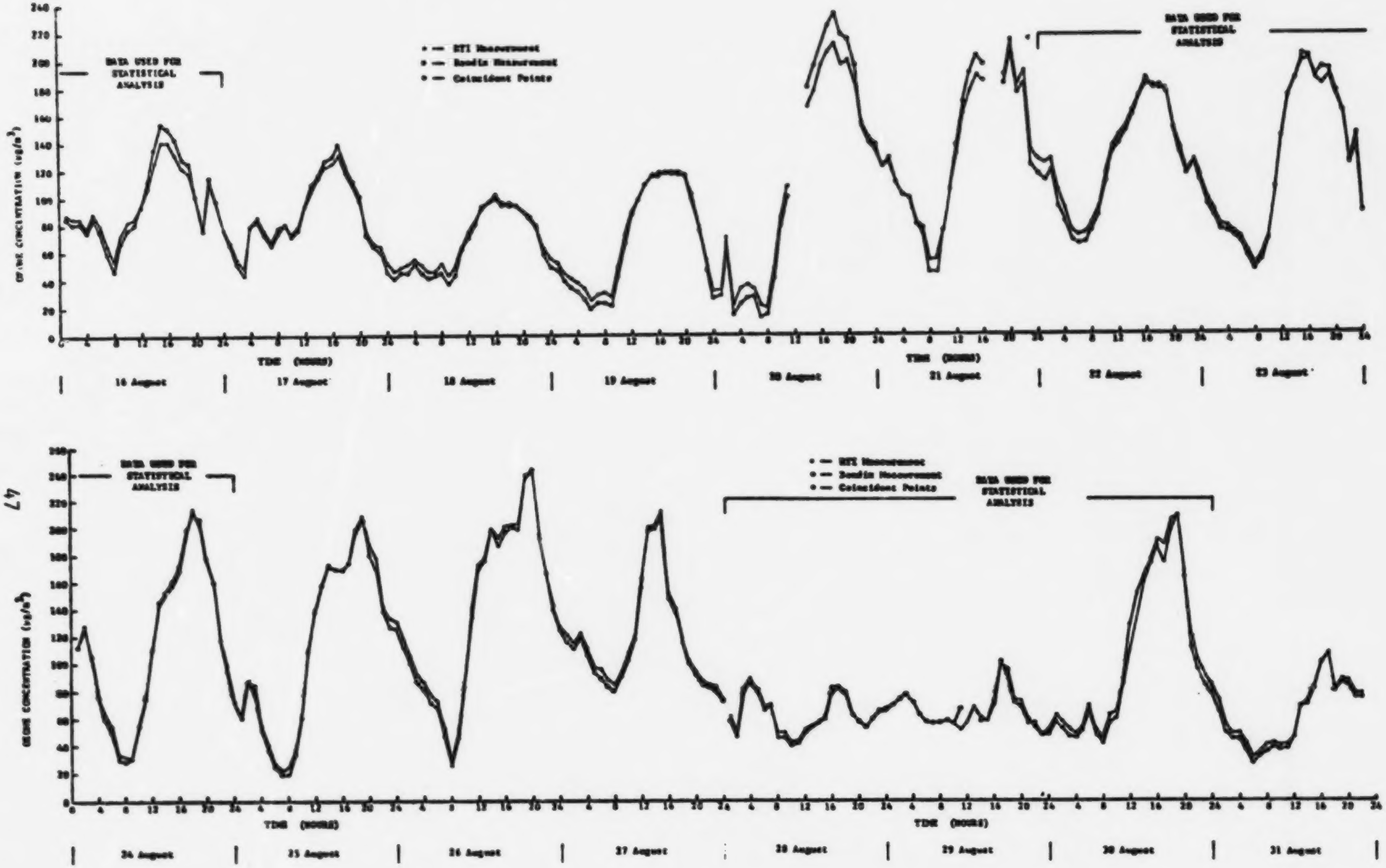


Figure 29. Comparison data for RTI solid phase and Bendix gas phase ozone analyzers.

instrument output. This facilitated the zero adjustment check of the recorders by allowing this operation to be carried out with a single switch. A digital voltmeter (DVM) was included for checking the instrument levels (and therefore checking the operation of the strip-chart recorders by checking the correctness of the deflection). The DVM could be switched to any instrument output with no movement of test leads.

Since there were up to five individual records represented--concentrations of O_3, NO, NO_2, NO_x and temperature--some means had to be utilized to correlate the five with each other and with the corresponding ground-level measurements. The zero adjust switch was used for this purpose. Each time a significant point was crossed in the flight pattern, the switch was activated causing all recorders to trace simultaneously to zero and return to normal leaving a distinguishable mark. The time of the event was marked on the ozone recorder to the nearest minute. The operator maintained a separate log of the times and the event which occurred. Since all recorders were run at the same chart speed, 20.3 cm/hr, the strip charts could be laid side by side and the time and location corresponding to any event determined.

The processing of the aircraft data was completely a manual operation. First, the strip charts were annotated with location information to determine which portions of the record contained data to be interpreted and which data were not valid (because of changing altitude, for example). Next, the trace deflection was measured for each strip chart and the appropriate scale applied to determine the represented concentration. The ozone data presented a somewhat special case, as both the measure cycle and calibrate cycle deflections are measured in terms of distance from the base line determined by trace during the purge cycle. The ozone concentration was computed from the following formula:

$$O_3 \text{ Conc } (\mu g/m^3) = C_{Gen} X \frac{M}{C}$$

where M is the measured deflection above base line of the strip chart during measure cycle.

C is the measured deflection above the base line of the strip-chart trace during calibration.

C_{Gen} is the concentration of the internal calibration unit determined during on-ground calibration.

X is the factor determined from the graphs giving response variation of the instrument with altitude.

After the data were converted to micrograms per cubic meter, they were placed on a map illustrating the flight path at the point corresponding to its origin. The flight path was drawn during the post flight debriefing of the pilot and copilot and using notes made by the meteorological observer. The data were then put on the map by observing where the particular data point fell on the strip chart in relation to noted significant events in the flight path (turns, prominent landmarks, etc.) and placing it on the pertinent portion of the flight path at a proportionate distance between the two nearest significant features. The times of all turns were placed on the maps as an aid to those who analyze the data. Oxides of nitrogen data were omitted, since they were generally below the detectable limits of the instrument.

Examples of selected aircraft flight paths with corresponding ozone data and positions for hydrocarbon grab samples are presented in Section 6.0, "Interpretation of Results." Data from all flights are presented in appendix C.

4.0 PROGRAM SCHEDULE

Details on the program schedule and the sequence of events that occurred during the period May 1, 1974, to August 31, 1974, are presented in this section. The overall program schedule as originally projected at the beginning of the program and presented in the "Work Plan" for Contract 68-02-1386, Task 4, is shown in table 4. Subsequent discussions related to the sequence of events that occurred in the ground station and aircraft measurement programs are presented in section 4.1, "Ground Station and Aircraft Measurement Program Schedule." Section 4.2 presents a brief discussion of the sequence of events that occurred during the "Quality Assurance Program," implemented in order to document and to insure the quality and validity of the data collected during this study.

4.1 Ground Station/Aircraft Measurement Program Schedule

The schedule presented in table 4 for each task was met with respect to acquisition/checkout/preparation of equipment for ground stations; site selection; preparation/installation/checkout of equipment in aircraft; installation of stations, analyzers, and equipment at designated sites; and calibration of all analyzers. Each of the five rural stations was set up, calibrated, and brought on line in a consecutive, orderly manner. The six urban stations were set up, calibrated, and brought on line by the Environmental Protection Agency during the week of June 10-15, 1974. The field measurement program began at all stations on or before June 15, 1974. The aircraft was ferried to Wilmington on schedule and subsequently prepared for routine aircraft flights, as dictated by meteorological conditions and the program plan. During the ensuing 75-day measurement program, dynamic calibrations were performed on each analyzer on a biweekly basis. Travel delays, instrument failures, and quality control/assurance procedures altered the schedule somewhat. Data acquisition continued through the end of August 1974.

Table 4. Program schedule

Date		Task
May 6, 1974		Start program/begin equipment acquisition.
	7	Begin preparation of comprehensive program plan.
	10	Receive government furnished equipment.
	11	Begin checkout of analyzers, recorders, etc.
	15-17	Select sites for ground stations.
	18	C-45 aircraft ferried to RDU/begin installation and checkout of systems.
June	6	Submit comprehensive program plan.
	7-10	Transport equipment from RTI to ground stations.
	3-14	Aircraft system test flights from RDU.
	12-14	Install, checkout, and calibrate equipment at monitoring stations.
	15	Begin field measurements at five rural stations.
	15	Begin field measurements at six urban stations (EPA).
July	1	Begin data reduction and analysis.
	3-8	Calibrate analyzers at each station.
	17-22	Calibrate analyzers at each station.
August	1-6	Calibrate analyzers at each station.
	15-21	Calibrate analyzers at each station.
	27-31	Calibrate analyzers at each station.
	31	Terminate field measurement program.
September	1-5	Disassemble equipment and monitoring sites and transport to Research Triangle Park. Return aircraft to NERC, Las Vegas.
	15-31	Continue data processing/reduction/begin statistical analysis of data.
October	1-31	Complete data processing/validate data.
	15-31	Continue statistical analysis of data/begin preparation of draft final report.
November	1-30	Complete data analysis/draft of final report.
	31	Submit draft of final report for EPA review.
December	15	Begin finalizing report.
	31	Receive EPA review of final report.
January 31, 1975		Submit final report.

During the 75-day field measurement program, a total of 19 aircraft flights were flown in support of ground-station measurements. These flights were flown under varying meteorological conditions and included square wave patterns, double box patterns, vertical profiles, calibration and instrument checkout flights, and an eastern wide-area flight. A listing of all flights is presented in table 5. A complete description of all flights with flight tracks, data, and meteorological summary is presented in appendix C.

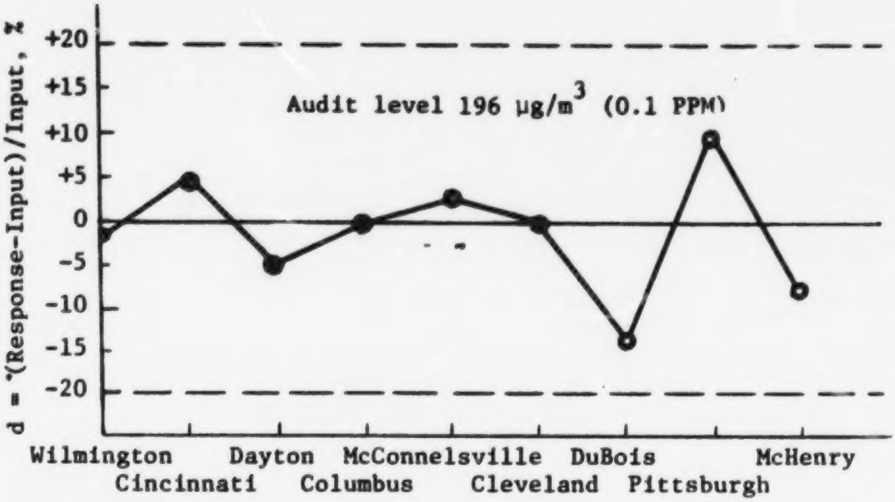
Table 5. Listing of aircraft flights

Date	Type of flight	Time	Flight altitude (meters)
20 June	Square Wave	1126--1245	610
25 June	Vertical Profile	0754--0934	to 3658
27 June	Square Wave	1131--1340	762
4 July	Square Wave	1148--1256	762
6 July	Double Box	1245--1719	762
9 July	Double Box	1026--1449	762
13 July	Double Box	1100--1518	762
16 July	Square Wave	1130--1403	914
17 July	Vertical Profile	1155--1321	to 2590
21 July	Square Wave	1158--1434	975
25 July	Square Wave	1308--1622	762
1 August	Vertical Profile	0704--0810	to 2438
1 August	Vertical Profile	0823--0913	to 1829
1 August	Vertical Profile	1320--1414	to 3658
1 August	Vertical Profile	1656--1822	to 3658
9 August	Batelle Comparison Flight	1502--1631	610
13 August	Vertical Over Morgan and Wayne County	1024--1406	762 to 2286
15 August	Vertical Profile	1053--1218	to 366
21 August	Eastern Flight	0939--1632	1219

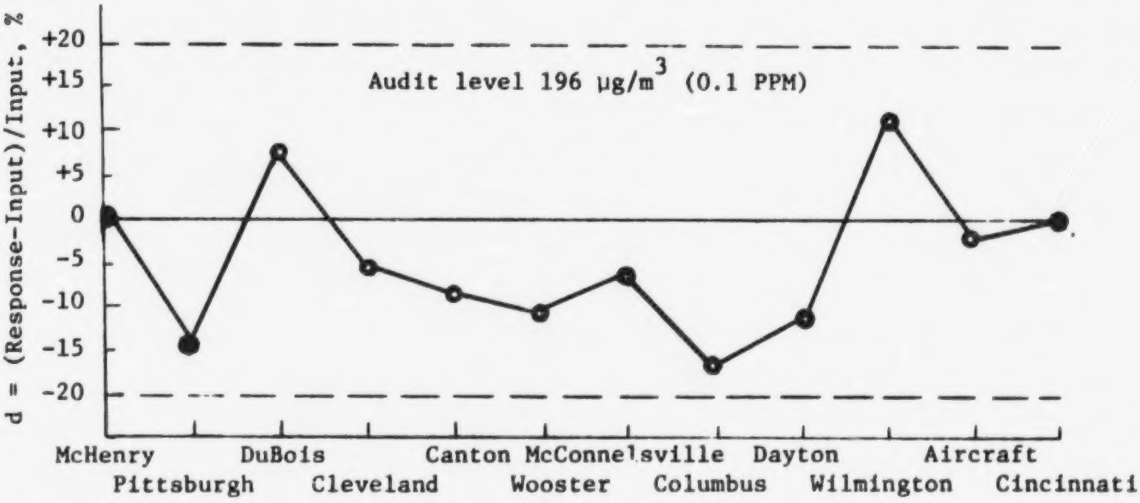
4.2 Quality Assurance Program

A quality assurance program was conducted as a separate task under Contract 68-02-1386 (Task 8) in order to assure, assess, and document the validity of the air quality measurements for the Summer 1974 Oxidant Study. Specific components of the quality assurance program included the following: (1) implementation of quality control procedures consisting of biweekly multipoint calibrations, daily zero and span checks, special operational checks, setting of action limits on checks and calibration; (2) certification of RTI and EPA calibration teams by the primary reference laboratory (i.e., Measurements Standardization Branch of National Environmental Research Center, Research Triangle Park) prior to beginning the field measurement program; and (3) onsite quality performance audits of the ozone, nitrogen dioxide, and hydrocarbon analyzers by a quality assurance team. The audit team utilized the same dynamic calibration techniques and apparatus as did the RTI and EPA calibration teams to provide reference samples to the ozone, nitrogen dioxide, and hydrocarbon analyzers. These calibration techniques and apparatus are described in appendix A.

During July and August 1974, four audits were performed at each of the rural and urban stations. Control charts were prepared, and the results for two of the audits are shown in figure 30. The ordinate of figure 30 is the percent difference in the analyzer response and the reference concentration, which was 196 $\mu g/m^3$ (0.1 ppm). The results of both audits shown in figure 30 indicate that the analyzer responses at all stations were within ± 20 percent of the reference value. Twenty percent at 196 $\mu g/m^3$ is the reproducibility of the method at the 95 percent level, as found in a collaborative test conducted by the Environmental Protection Agency.[9/] Analyzer responses to the audit concentrations of nitrogen dioxide at the five rural stations were within ± 20 percent or better of the reference value. Audits of the hydrocarbon analyzers at Wilmington, McConnelsville, and Wooster indicated that in all cases methane was measured to within 13 percent of the assayed value and total hydrocarbon measured as methane to within 21 percent or better. Audit of the EPA Perkin-Elmer model 900 gas chromatograph system at Wilmington indicated measurements of better than 15 percent for all compounds contained in the audit hydrocarbons samples.



AUDIT OF O_3 ANALYZERS BY RTI AND EPA CALIBRATION TEAMS (JULY 15-25)



AUDIT OF O_3 ANALYZERS BY RTI AUDIT TEAM (AUGUST 15-21)

Figure 30. Results of audits of ozone analyzers at stations during period July 15-25, 1974, and August 15-21, 1974.

The results of the quality assurance/audit program have demonstrated that the air-quality measurements obtained during the Summer 1974 Oxidant Study are valid and that the performance audit results represent realistic estimates of the accuracy and precision of these measurements for the concentration levels audited. The details of the Quality Assurance Program are documented in the final report for Contract 68-02-1386, Task 8, "Quality Assurance Program Relative to Summer 1974 Oxidant Study."[10]

5.0 SUMMARY OF DATA AND STATISTICS

The results of the field measurement program are presented in this section and include summary statistics, diurnal pollutant-concentration patterns, and a meteorological summary for June, July, and August 1974. Ozone and hydrocarbon data from three diurnal studies at Wilmington, hydrocarbon analyses of grab samples at Wilmington, Wooster, and McConnelsville, and concentrations of ozone and hydrocarbons, and pertinent ratios of compounds in grab samples collected during aircraft flights are not presented here, but are summarized in section 6.0 in order to facilitate discussion and interpretation of these results.

5.1 Summary Statistics

Mean hourly ozone concentrations, standard deviations, and case counts by station are shown in table 6, and ozone data above the NAAQS for photochemical oxidant are summarized in table 7. Statistical data for nitrogen dioxide and total hydrocarbon, methane, and carbon monoxide concentrations by station are presented in tables 8 and 9, respectively.

Table 6. Statistical summary of hourly ozone concentration measurements by station June 14-August 31, 1974

Station	Mean hourly concentration ($\mu g/m^3$)	Standard deviation ($\mu g/m^3$)	Case count
Wilmington, Ohio	103	55	1751
McConnelsville, Ohio	102	48	1801
Wooster, Ohio	94	59	1878
McHenry, Maryland	113	45	2011
DuBois, Pennsylvania	112	63	1667
Canton, Ohio*	71	56	1829
Cincinnati, Ohio*	49	54	1548
Cleveland, Ohio*	62	48	1652
Columbus, Ohio*	65	64	1935
Dayton, Ohio*	71	56	1576
Pittsburgh, Pennsylvania*	56	56	1622

*Urban stations

Table 7. Summary of ozone data above NAAQS by station (June 14-August 31, 1974).

Station	Maximum hourly average concentration ($\mu g/m^3$)	99th percentile ($\mu g/m^3$)	Days exceeding standard (%)[1]	Hours above standard (number)	Hours above standard (%)
Wilmington, Ohio*	370	260	58	259	14.9
McConnelsville, Ohio*	330	240	56	239	13.3
Wooster, Ohio*	330	260	55	262	14.0
McHenry, Maryland*	330	270	43	262	13.0
DuBois, Pennsylvania*	400	310	54	341	20.5
Canton, Ohio**	280	230	44	148	8.0
Cincinnati, Ohio**	360	220	20	54	3.5
Cleveland, Ohio**	270	200	26	51	3.0
Columbus, Ohio**	340	220	27	113	5.8
Dayton, Ohio**	260	220	35	114	7.2
Pittsburgh, Pennsylvania**	300	230	37	106	6.5

*Rural stations
**Urban stations

[1] Based on data available from each station

Table 8. Statistical summary of hourly nitrogen dioxide concentration measurements by station (June 14-August 31, 1974).

Station	Mean hourly concentration ($\mu g/m^3$)	Standard deviation ($\mu g/m^3$)	Case count
Wilmington, Ohio	13	24	1741
McConnelsville, Ohio	12	34	1775
Wooster, Ohio	13	15	1889
McHenry, Maryland	11	6	2017
DuBois, Pennsylvania	19	9	1971

Table 9. Statistical summary of hourly total hydrocarbon, methane, and carbon monoxide concentration measurements by station (June 14-August 31, 1974).

Station	Parameter	Mean hourly concentration ($\mu g/m^3$)	Standard deviation ($\mu g/m^3$)	Case count
Wilmington, Ohio	THC	1180	300	831
	CH_4	1120	310	811
	CO	330	460	980
	NMHC*	60		
McConnelsville, Ohio	THC	1260	130	754
	CH_4	1040	380	707
	CO	230	90	244
	NMHC*	220		
Wooster, Ohio	THC	1360	300	849
	CH_4	1170	340	831
	CO	200	200	793
	NMHC*	190		

*NMHC = THC - CH_4

The mean hourly concentrations for ozone at the rural stations ranged from 94 to 113 $\mu g/m^3$, as opposed to a range of 49 to 71 $\mu g/m^3$ at the urban stations. The standard deviations for all stations, both rural and urban, were, however, similar in magnitude (see table 6). Maximum hourly ozone concentrations were 370 $\mu g/m^3$ at Wilmington, 330 $\mu g/m^3$ at McConnelsville, 330 $\mu g/m^3$ at Wooster, Ohio; 330 $\mu g/m^3$ at McHenry, Maryland; 400 $\mu g/m^3$ at DuBois, Pennsylvania; 280 $\mu g/m^3$ at Canton, 360 $\mu g/m^3$ at Cincinnati, 270 $\mu g/m^3$ at Cleveland, 340 $\mu g/m^3$ at Columbus, 260 $\mu g/m^3$ at Dayton, Ohio; and 300 $\mu g/m^3$ at Pittsburgh, Pennsylvania.

The data summarized in table 7 show that the NAAQS for photochemical oxidants (160 $\mu g/m^3$) was exceeded during approximately 15, 13, 14, 13, and 21 percent of the hours at the rural stations (i.e., Wilmington, McConnelsville, Wooster, Ohio; McHenry, Maryland, and DuBois, Pennsylvania) and approximately 8, 4, 3, 6, 7, and 7 percent of the hours at the urban stations (i.e., Canton, Cincinnati, Cleveland, Columbus, Dayton, Ohio; and

Pittsburgh, Pennsylvania), respectively. These data also show that the NAAQS for photochemical oxidant was exceeded approximately twice as frequently at rural stations as at urban stations, both in terms of percent of days and percent of hours.

The mean hourly concentrations of nitrogen dioxide at the five rural stations ranged from 11 to 19 $\mu g/m^3$ and was slightly above the detectability level of the measurement method ($\approx$ 10 $\mu g/m^3$). Maximum hourly nitrogen dioxide concentrations were 90 $\mu g/m^3$ at Wilmington; 70 $\mu g/m^3$ at McConnelsville; 90 $\mu g/m^3$ at Wooster, Ohio; 60 $\mu g/m^3$ at McHenry, Maryland; and 70 $\mu g/m^3$ at DuBois, Pennsylvania. The mean hourly concentrations for nonmethane hydrocarbon ($THC-CH_4$) were approximately 60 $\mu g/m^3$ at Wilmington, 220 $\mu g/m^3$ at McConnelsville, and 190 $\mu g/m^3$ at Wooster for the measurement period. Maximum hourly nonmethane hydrocarbon concentrations were 120 $\mu g/m^3$ at Wilmington; 280 $\mu g/m^3$ at McConnelsville; and 280 $\mu g/m^3$ at Wooster. Mean hourly carbon monoxide concentrations ranged from approximately 200 $\mu g/m^3$ at Wooster and McConnelsville to 325 $\mu g/m^3$ at Wilmington. Maximum hourly carbon monoxide concentrations were 480 $\mu g/m^3$ at Wilmington; 270 $\mu g/m^3$ at McConnelsville; and 260 $\mu g/m^3$ at Wooster.

The data presented in tables 8 and 9 were used to compute the nonmethane hydrocarbon ($NMHC = THC-CH_4)/NO_2$ ratio (ppm carbon/ppm NO_2) at each station. The ratios of $NMHC/NO_2$ for the measurement period are:

1. Wilmington, Ohio: 13*,
2. McConnelsville, Ohio: 53*,
3. Wooster, Ohio: 42*.

The low ratio found at Wilmington, Ohio, (13) is more nearly characteristic of urban ratios, while the higher ratios at McConnelsville and Wooster, Ohio, are representative of what would be expected in rural environments.

Cumulative frequency distributions for hourly ozone concentrations by station are presented for the entire period in table 10. Cumulative frequency distributions for hourly nitrogen dioxide concentrations are presented in table 11. Cumulative frequency distributions of hourly total hydrocarbon, methane, and carbon monoxide concentrations are presented in table 12.

---

*Molar Ratios = ppm C/ppm NO_2

Table 10. Cumulative frequency distributions of hourly concentration of ozone by station (June 14-August 31, 1974)

Concentrations ($\mu g/m^3$)	Percent of samples greater than stated concentration										
	Wilmington, Ohio	McConnelsville, Ohio	Wooster, Ohio	McHenry, Maryland	DuBois Pennsylvania	Canton,* Ohio	Cincinnati,* Ohio	Cleveland,* Ohio	Columbus,* Ohio	Dayton,* Ohio	Pittsburgh* Pennsylvania
0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
10	99.9	99.9	99.4	100.0	99.9	95.5	71.1	88.1	85.3	88.5	81.3
20	99.3	99.9	96.5	100.0	99.0	84.3	62.7	82.0	76.9	81.4	71.3
30	97.7	99.4	93.8	99.8	97.4	76.2	55.0	74.8	69.0	74.5	62.0
40	94.1	97.1	88.1	99.5	94.5	71.9	48.2	66.2	61.6	67.1	53.2
50	89.1	92.4	81.0	97.8	90.5	60.6	42.4	57.3	54.8	60.7	45.5
60	82.5	86.1	72.9	95.9	85.1	53.0	34.9	50.1	47.5	55.0	40.5
70	76.4	78.5	65.7	91.7	78.4	47.9	30.9	42.6	42.6	48.1	35.2
80	69.6	70.2	60.1	86.1	71.0	42.5	27.3	35.5	37.7	42.5	30.2
90	62.3	61.2	51.4	75.1	63.9	36.9	23.4	29.8	33.5	37.5	26.7
100	54.1	54.1	45.3	64.7	56.4	32.2	21.3	24.8	28.9	33.3	23.1
110	46.7	46.9	39.3	54.7	49.7	27.2	18.7	20.1	24.5	28.3	20.7
120	40.5	39.9	34.5	45.8	44.1	23.7	15.6	16.7	21.1	24.0	16.8
130	34.4	33.9	28.2	37.2	39.4	20.3	12.5	13.6	17.7	19.8	13.9
140	28.8	28.2	23.9	30.3	34.0	16.7	9.5	9.9	13.7	15.0	11.0
150	24.0	22.6	20.5	18.2	29.0	13.3	7.8	7.1	10.5	11.8	9.0
160	19.4	17.5	17.4	13.0	24.8	10.9	5.5	4.8	7.2	9.5	7.4
170	16.5	13.4	14.9	9.1	20.5	8.2	3.6	3.3	5.8	7.4	5.7
180	13.0	9.7	12.9	7.2	17.6	6.3	2.5	2.1	4.3	5.3	4.6
190	10.1	6.6	10.8	5.6	13.7	5.4	1.7	1.6	3.3	3.9	3.8
200	8.1	4.3	8.6	4.3	11.8	4.2	1.4	1.2	2.1	2.8	2.8
210	5.4	3.1	6.4	3.4	10.0	2.4	1.2	0.7	1.6	1.9	2.3
220	2.7	2.3	4.4	2.9	8.0	1.4	0.8	0.5	1.2	1.5	1.4
230	2.2	1.5	3.1	2.2	5.7	0.9	0.6	0.3	0.8	0.9	1.2
240	1.4	0.8	2.1	1.8	4.6	0.7	0.5	0.2	0.7	0.4	1.0
250	1.1	0.3	1.2	1.4	4.0	0.4	0.5	0.1	0.6	0.1	0.7
260	0.9	0.2	0.7	1.2	3.2	0.4	0.4	0.1	0.5	0.1	0.6
270	0.6	0.1	0.5	0.8	2.6	0.2	0.3	0.1	0.4	0.0	0.4
280	0.6	0.1	0.4	0.3	1.8	0.1	0.2	0.0	0.3	0.0	0.2
290	0.5	0.1	0.3	0.3	1.4	0.0	0.2	0.0	0.3	0.0	0.2
300	0.3	0.1	0.2	0.2	1.1	0.0	0.1	0.0	0.3	0.0	0.1
310	0.2	0.1	0.2	0.2	1.0	0.0	0.1	0.0	0.2	0.0	0.0
320	0.2	0.1	0.1	0.2	0.9	0.0	0.1	0.0	0.2	0.0	0.0
330	0.2	0.1	0.1	0.1	0.8	0.0	0.1	0.0	0.2	0.0	0.0
340	0.1	0.0	0.0	0.0	0.7	0.0	0.1	0.0	0.1	0.0	0.0
350	0.1	0.0	0.0	0.0	0.6	0.0	0.1	0.0	0.0	0.0	0.0
360	0.1	0.0	0.0	0.0	0.4	0.0	0.1	0.0	0.0	0.0	0.0
370	0.1	0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0
380	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0
390	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
400	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
410	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
420	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
430	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
440	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
450	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
460	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
470	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
480	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
490	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
500	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

*Urban stations

Table 11. Cumulative frequency distributions of hourly concentrations of nitrogen dioxide by station (June 14-August 31, 1974).

Concentration ($\mu g/m^3$)	Percent of samples greater than stated concentration				
	Wilmington, Ohio	McConnelsville, Ohio	Wooster, Ohio	McHenry, Maryland	DuBois, Pennsylvania
	100.0	100.0	100.0	100.0	100.0
0	96.7	98.5	81.0	99.7	98.1
10	45.5	45.6	44.4	47.4	42.1
20	14.9	5.6	23.8	6.9	13.2
30	5.1	1.4	13.4	1.1	3.7
40	2.6	0.5	6.9	0.2	1.0
50	1.6	0.3	3.7	0.1	0.6
60	1.1	0.1	1.9	0.1	0.2
70	1.0	0.1	0.5	0.0	0.1
80	0.5	0.0	0.3	0.0	0.0
90	0.1	0.0	0.1	0.0	0.0
100	0.0	0.0	0.0	0.0	0.0

Table 12. Cumulative frequency distributions of hourly concentrations of total hydrocarbon, methane, and carbon monoxide by station (June 14-August 31, 1974)

Concentration		Percent of samples greater than stated concentration								
($\mu g/m^3$)		Wilmington, Ohio			McConnelsville, Ohio			Wooster, Ohio		
THC/CH_4	CO	THC	CH_4	CO	THC	CH_4	CO	THC	CH_4	CO
		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
800	0	98.8	98.8	100.0	100.0	95.5	100.0	100.0	95.8	98.9
850	50	98.7	98.8	100.0	100.0	90.2	99.6	100.0	93.1	77.9
900	100	98.4	98.5	99.6	100.0	81.6	95.5	100.0	91.8	68.2
950	150	98.4	98.4	92.7	100.0	68.9	82.0	100.0	89.2	54.7
1000	200	95.3	96.8	62.4	100.0	57.1	60.2	99.9	85.8	39.6
1050	250	84.1	79.0	41.7	98.8	43.4	38.1	97.2	78.8	29.0
1100	300	67.0	38.1	21.8	92.8	28.0	22.5	84.3	62.8	18.5
1150	350	39.2	11.1	15.2	83.2	12.0	11.5	82.0	49.8	13.2
1200	400	27.0	5.5	9.2	67.0	5.9	2.9	72.0	35.5	10.5
1250	450	16.6	3.9	6.4	47.7	3.8	1.6	61.0	23.6	7.2
1300	500	11.1	3.6	5.6	30.8	3.1	0.0	50.6	16.2	6.3
1350	550	7.0	3.6	5.3	18.3	2.3	0.0	39.7	11.7	4.7
1400	600	5.3	3.3	5.3	10.3	1.7	0.0	32.2	8.1	3.0
1450	650	4.2	3.2	4.9	6.2	1.1	0.0	26.6	6.0	2.4
1500	700	4.0	3.2	4.9	3.4	0.7	0.0	21.4	5.1	1.9
1550	750	4.0	3.2	4.6	1.5	0.6	0.0	18.1	3.9	1.6
1600	800	3.4	3.1	4.5	0.9	0.6	0.0	14.6	3.4	1.3
1650	850	3.4	2.8	4.5	0.9	0.6	0.0	11.9	2.8	0.8
1700	900	3.1	2.8	4.4	0.8	0.6	0.0	10.0	2.2	0.4
1750	950	3.1	2.7	4.3	0.8	0.4	0.0	8.4	1.7	0.1
1800	1000	3.1	2.7	4.2	0.8	0.2	0.0	6.6	1.7	0.0
1850	1050	2.8	2.6	3.4	0.7	0.1	0.0	4.5	1.6	0.0
1900	1100	2.8	2.6	2.9	0.5	0.0	0.0	2.8	1.3	0.0
1950	1150	2.8	1.2	2.8	0.3	0.0	0.0	1.8	1.1	0.0
2000	1200	2.8	1.2	2.8	0.1	0.0	0.0	1.4	0.8	0.0

5.2 Diurnal Patterns

Mean ozone concentrations for each hour of the day by station for the period June 14 through August 31, 1974, are shown in table 13. Mean nitrogen dioxide, total hydrocarbon, methane, nonmethane hydrocarbon, and carbon monoxide concentrations for each hour of the day by station are presented in table 14. Mean diurnal curves for ozone are shown for rural and urban stations in figures 31-34. Figures 31 and 32 present the mean diurnal curves for Wilmington, McConnelsville, Wooster, and Wilmington, McHenry, and DuBois, respectively. Mean diurnal ozone curves for the cities of Canton, Cincinnati, and Cleveland are presented in figure 33 and for the cities of Columbus, Dayton, and Pittsburgh in figure 34. The mean diurnal ozone curves for the rural and urban stations show the same general pattern; however, several differences can be noted as follows:

1. Mean hourly ozone concentrations for rural stations range from approximately 40 $\mu g/m^3$ during early morning hours to 140-160 $\mu g/m^3$ in the afternoon, while for urban stations, the mean ranges from 15-25 $\mu g/m^3$ to 100-125 $\mu g/m^3$.
2. Mean hourly ozone concentrations tend to peak later in the afternoon at rural sites (see table 13). This observation is further discussed in section 6.2.
3. The overall range or spread of mean ozone concentrations for both rural and urban stations from low to high was approximately the same (i.e., 100-125 $\mu g/m^3$) during this period of time.

Figure 35 contrasts the mean diurnal ozone concentration curves for 1972, 1973, and 1974 at McHenry, Maryland. Figure 35 shows that the 1972 and 1974 diurnal curves are almost identical, while the 1973 concentrations are somewhat higher. The difference between the 1972, 1974 curves and the 1973 curve can be attributed to differences in meteorological conditions.

Mean diurnal curves for nitrogen dioxide concentration for each station are presented in figure 36. Mean diurnal concentrations for total hydrocarbon, methane, and carbon monoxide are presented in

Table 13. Means of hourly concentrations of ozone for each hour of day
(June 14-August 31, 1974)

	Concentration ($\mu g/m^3$)										
Hour	Wilmington, Ohio	McConnelsville, Ohio	Wooster, Ohio	McHenry, Maryland	DuBois, Pennsylvania	Canton, Ohio	Cincinnati, Ohio	Cleveland, Ohio	Columbus, Ohio	Dayton, Ohio	Pittsburgh, Pennsylvania
0100	85.2	95.4	67.6	109.7	97.4	42.6	13.3	45.5	36.6	38.2	24.2
0200	79.3	87.9	60.9	107.4	91.8	43.4	16.1	44.9	36.0	36.6	22.9
0300	73.4	84.6	55.2	104.6	85.1	43.3	17.4	44.5	33.5	36.1	26.0
0400	67.7	73.3	51.6	103.0	79.3	40.5	18.0	45.8	32.6	34.0	28.6
0500	61.6	67.7	49.1	100.3	72.6	37.4	14.0	42.7	31.4	32.6	24.8
0600	55.9	61.1	45.0	98.7	67.3	31.1	8.9	35.5	30.4	24.0	22.0
0700	52.1	55.6	40.8	96.5	61.2	25.2	7.5	27.1	17.0	19.6	15.9
0800	50.3	51.5	40.6	93.4	62.7	20.8	15.2	26.7	18.0	18.8	14.1
0900	61.9	56.2	54.1	91.3	73.6	30.8	26.8	30.6	19.0	24.9	19.2
1000	77.7	69.7	72.7	95.8	84.5	48.1	49.2	45.0	41.1	43.7	32.5
1100	95.7	88.2	93.2	103.5	106.6	71.7	75.1	58.3	60.7	69.4	50.0
1200	117.9	110.7	114.6	113.4	125.5	93.3	91.3	73.6	81.7	97.1	68.1
1300	133.6	125.7	128.6	120.3	137.0	106.3	102.1	88.0	99.9	113.9	93.8
1400	142.4	136.5	134.3	123.6	148.8	116.2	111.9	101.4	111.9	121.3	114.9
1500	152.9	141.1	143.5	128.0	159.0	123.6	112.7	100.3	120.0	127.0	118.1
1600	152.6	146.3	146.0	131.0	160.9	122.7	109.3	106.9	120.4	129.1	124.9
1700	156.3	147.1	142.7	131.7	161.2	123.6	105.1	104.2	124.8	134.5	
1800	154.3	142.5	153.2	129.7	158.2	121.9	94.7	102.8	130.1	129.5	113.0
1900	152.5	140.0	150.5	128.3	154.2	116.8	77.5	95.4	113.5	124.0	103.8
2000	143.9	133.4	138.7	125.6	142.3	104.5	50.1	83.3	74.0	112.4	84.6
2100	125.3	119.6	116.8	122.0	128.2	80.1	30.8	67.0	54.1	84.6	57.6
2200	109.0	109.9	98.4	118.7	119.2	60.0	21.0	48.6	54.1	56.3	40.9
2300	98.9	106.9	85.6	116.1	109.2	46.4	16.1	42.5	41.2	44.9	36.8
2400	89.5	101.9	74.9	111.1	101.3	42.8	14.2	41.6	39.0	45.3	28.1

Table 14. Means of hourly concentrations of nitrogen dioxide, total hydrocarbons, methane, and carbon monoxide for each hour of day (June 14-August 31, 1974)

	Concentration ($\mu g/m^3$)														
	Wilmington, Ohio				McConnelsville, Ohio				Wooster, Ohio				McHenry, Maryland*	DuBois, Pennsylvania*
Hour	NO_2	THC	CH_4	CO	NO_2	THC	CH_4	CO	NO_2	THC	CH_4	CO	NO_2	NO_2
0100	14.3	1172.5	1109.1	294.6	10.9	1234.2	1043.1	225.4	19.4	1397.4	1153.9	219.5	10.7	12.1
0200	11.8	1184.9	1121.9	256.4	11.0	1252.4	1027.5	226.3	19.0	1403.5	1177.1	211.6	11.0	12.6
0300	11.4	1200.3	1128.0	265.3	10.5	1261.4	1039.3	227.3	19.4	1435.7	1186.2	210.1	10.7	13.8
0400	11.8	1208.2	1130.0	267.3	10.7	1277.2	1039.0	225.6	18.0	1469.2	1211.5	188.4	10.1	14.4
0500	12.5	1210.1	1134.4	269.4	10.8	1304.7	1037.4	242.5	15.7	1474.5	1232.9	178.4	10.2	14.1
0600	12.9	1219.6	1139.2	270.0	10.9	1311.1	1065.6	242.5	15.4	1467.4	1259.8	175.7	9.5	14.5
0700	13.4	1234.4	1151.1	273.9	11.8	1315.7	1266.2	265.6	16.9	1523.2	1299.4	195.0	9.8	15.3
0800	15.7	1230.9	1153.0	279.8	11.9	1318.1	1080.2	245.9	17.6	1556.6	1460.7	210.2	10.8	14.8
0900	16.7	1239.3	1141.7	304.0	12.2	1348.7	1081.5	242.4	17.0	1495.1	1219.3	234.1	11.1	13.9
1000	17.1	1211.8	1132.1	395.2	12.9	1361.1	1188.9	241.0	15.4	1373.0	1313.1	240.1	11.3	13.5
1100	20.5	1130.3	1099.5	380.9	12.5	1301.5	1016.0	256.4	11.8	1331.9	1126.4	225.9	11.8	11.8
1200	15.1	1101.5	1055.4	333.7	11.4	1273.1	1018.2	248.0	9.9	1273.8	1111.1	181.1	10.6	9.5
1300	11.5	1178.4	1155.1	439.4	10.3	1234.9	979.1	223.6	7.5	1233.9	1116.[illegible]	156.3	9.9	8.2
1400	11.7	1159.3	1118.8	473.8	10.4	1208.3	977.0	213.3	7.1	1209.8	1092.4	147.2	10.8	6.8
1500	8.1	1145.9	1093.1	414.0	9.0	1203.4	982.3	216.2	5.6	1196.2	1127.1	143.2	9.5	5.8
1600	7.7	1158.7	1068.3	353.3	5.5	1215.7	968.8	206.6	4.9	1210.8	1049.1	201.1	9.3	5.5
1700	16.3	1242.4	1120.5	353.0	8.8	1205.8	1209.0	195.3	5.4	1183.3	1136.5	255.5	9.1	5.6
1800	14.4	1200.6	1216.3	355.2	8.0	1208.4	960.2	202.6	5.1	1192.4	1063.1	143.0	9.5	5.8
1900	8.4	1177.4	1079.0	328.3	22.1	1202.3	951.7	199.1	6.5	1226.0	1065.4	154.7	10.1	6.0
2000	6.9	1245.0	1268.1	296.0	22.2	1197.1	1031.8	239.7	9.6	1266.4	1075.9	199.6	10.2	7.3
2100	8.5	1145.3	1099.0	338.7	10.3	1260.4	979.6	250.7	13.9	1302.7	1102.3	226.9	10.8	8.8
2200	10.6	1154.6	1095.8	249.2	12.9	1229.2	995.7	236.1	18.3	1356.8	1134.6	239.0	11.5	10.6
2300	16.7	1141.4	1088.2	306.4	11.3	1218.6	1012.4	241.9	18.7	1402.4	1181.1	232.9	11.6	12.2
2400	18.8	1159.7	1097.1	309.0	11.3	1232.0	1008.0	234.5	19.6	1390.0	1147.5	219.6	12.3	12.5

*THC, CH_4, CO NOT MEASURED

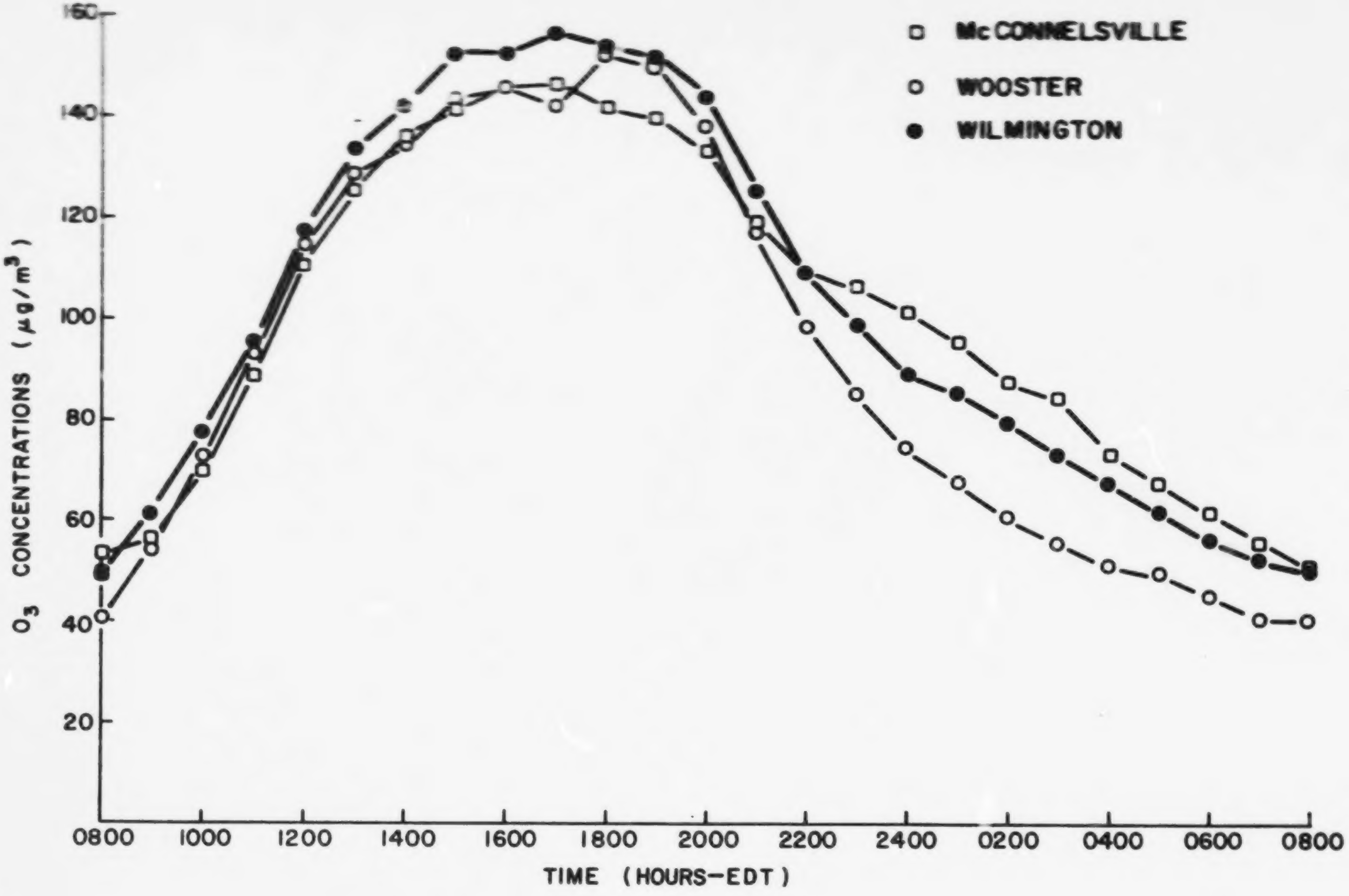


Figure 31. Mean diurnal ozone concentration at Wilmington, Wooster, and McConnelsville, Ohio, from June 15-August 31, 1974.

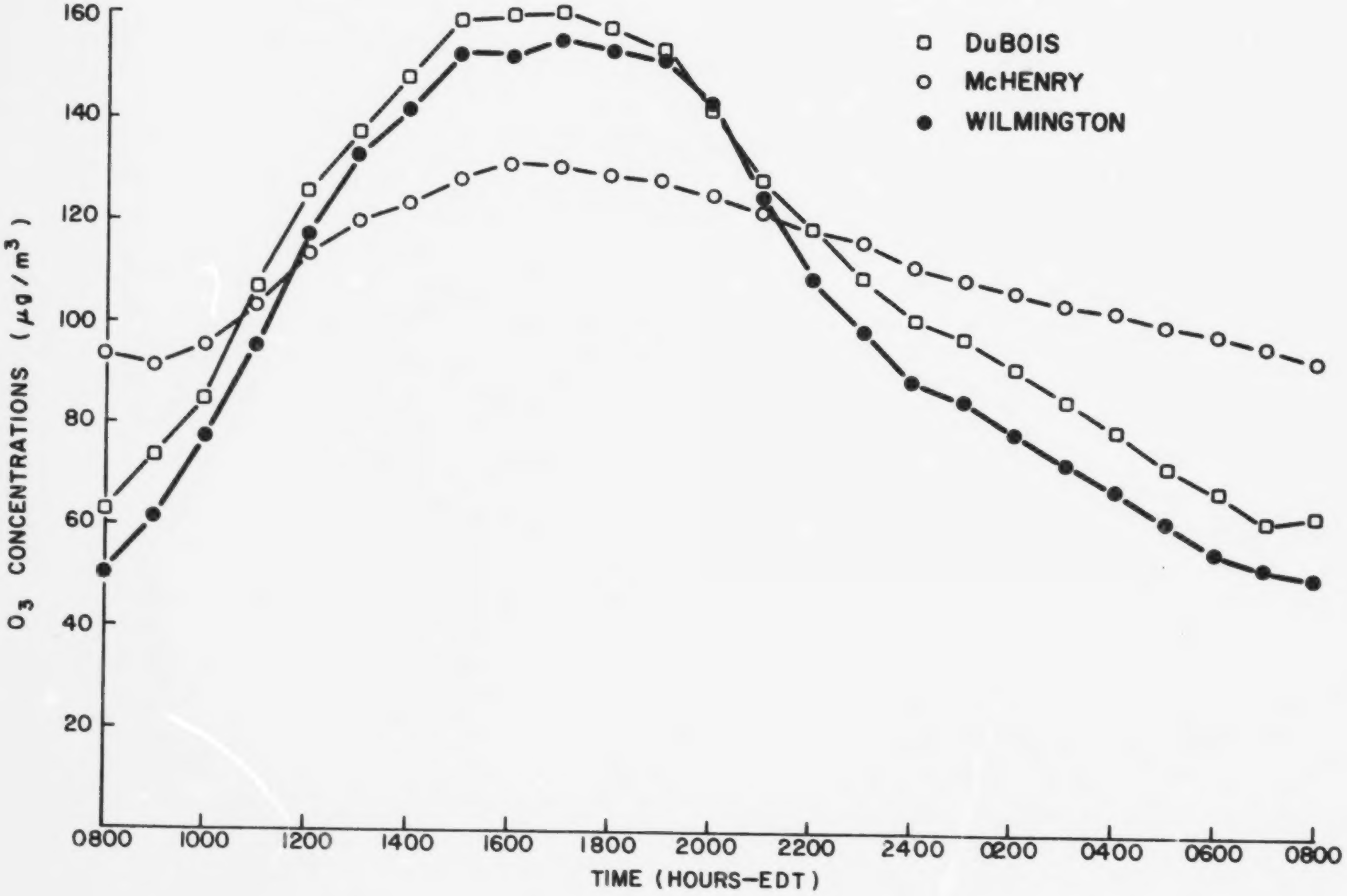


Figure 32. Mean diurnal ozone concentration at Wilmington, Ohio; DuBois, Pennsylvania; and McHenry, Maryland from June 14-August 31, 1974.

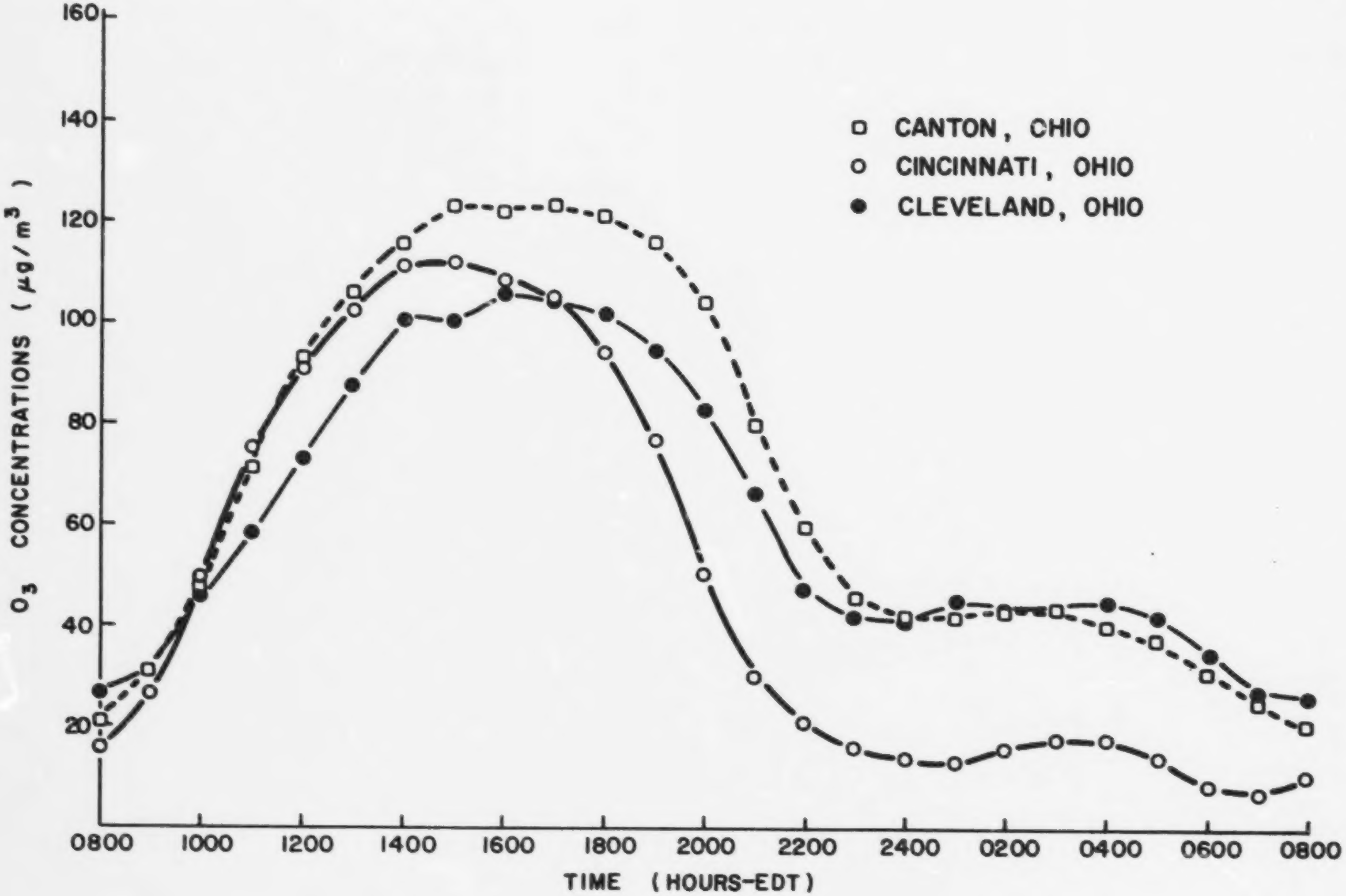


Figure 33. Mean diurnal ozone concentration for Canton, Cincinnati, and Cleveland, Ohio from June 14-August 31, 1974.

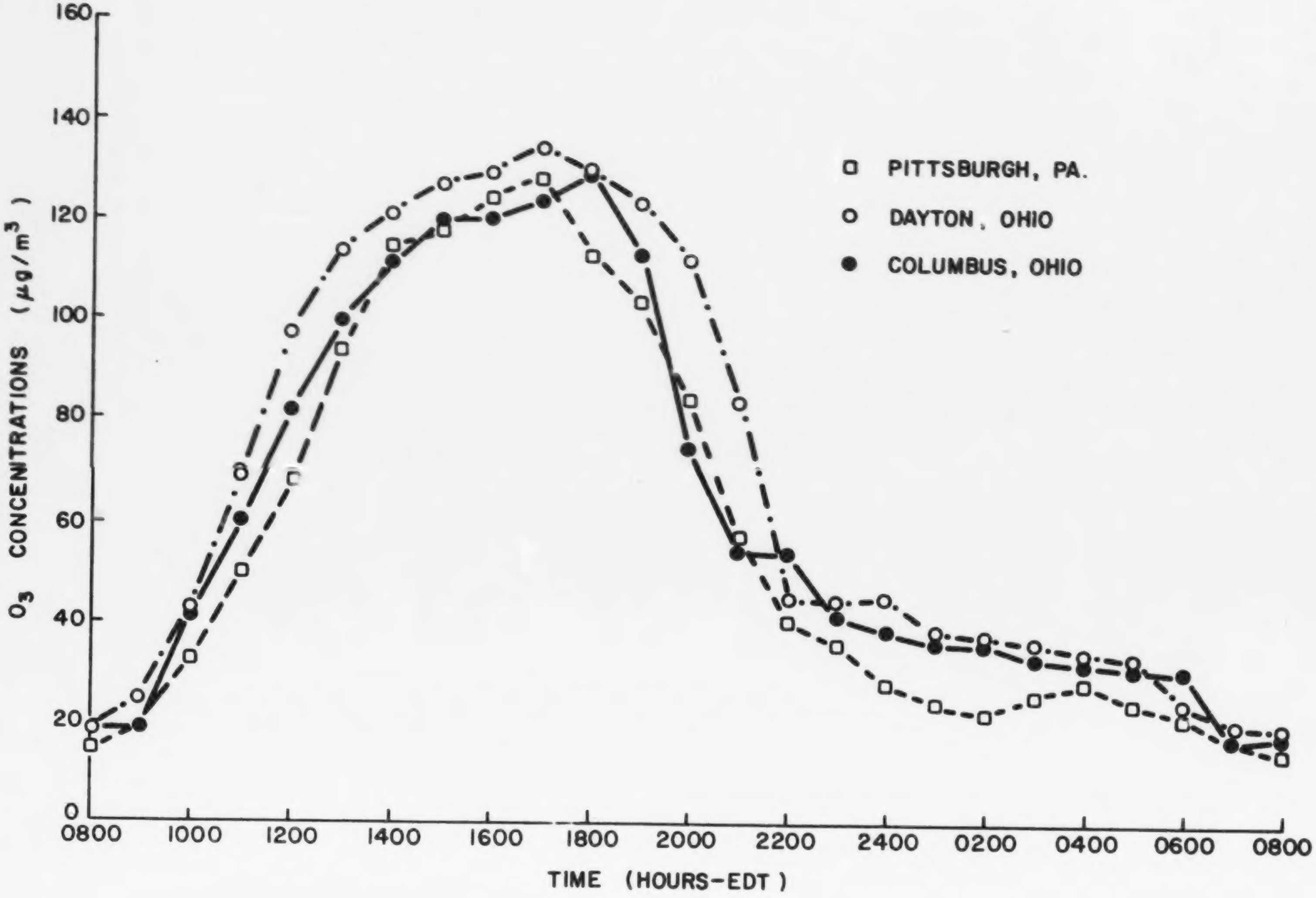


Figure 34. Mean diurnal ozone concentration for Columbus and Dayton, Ohio; and Pittsburgh, Pennsylvania from June 14-August 31, 1974.

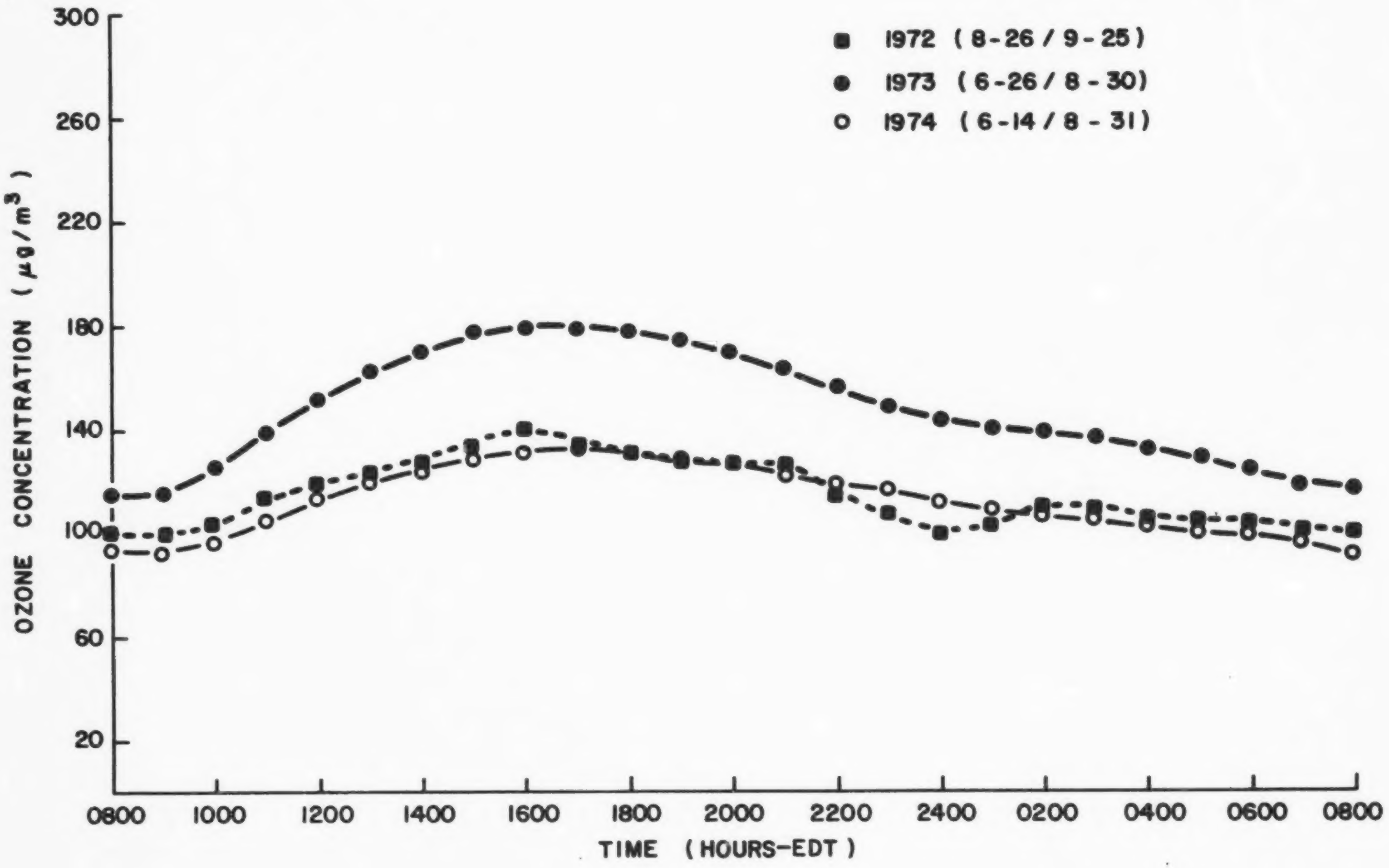


Figure 35. Mean Diurnal Ozone Concentration at McHenry (Garrett County Airport) Station for 1972. 1973, and 1974.

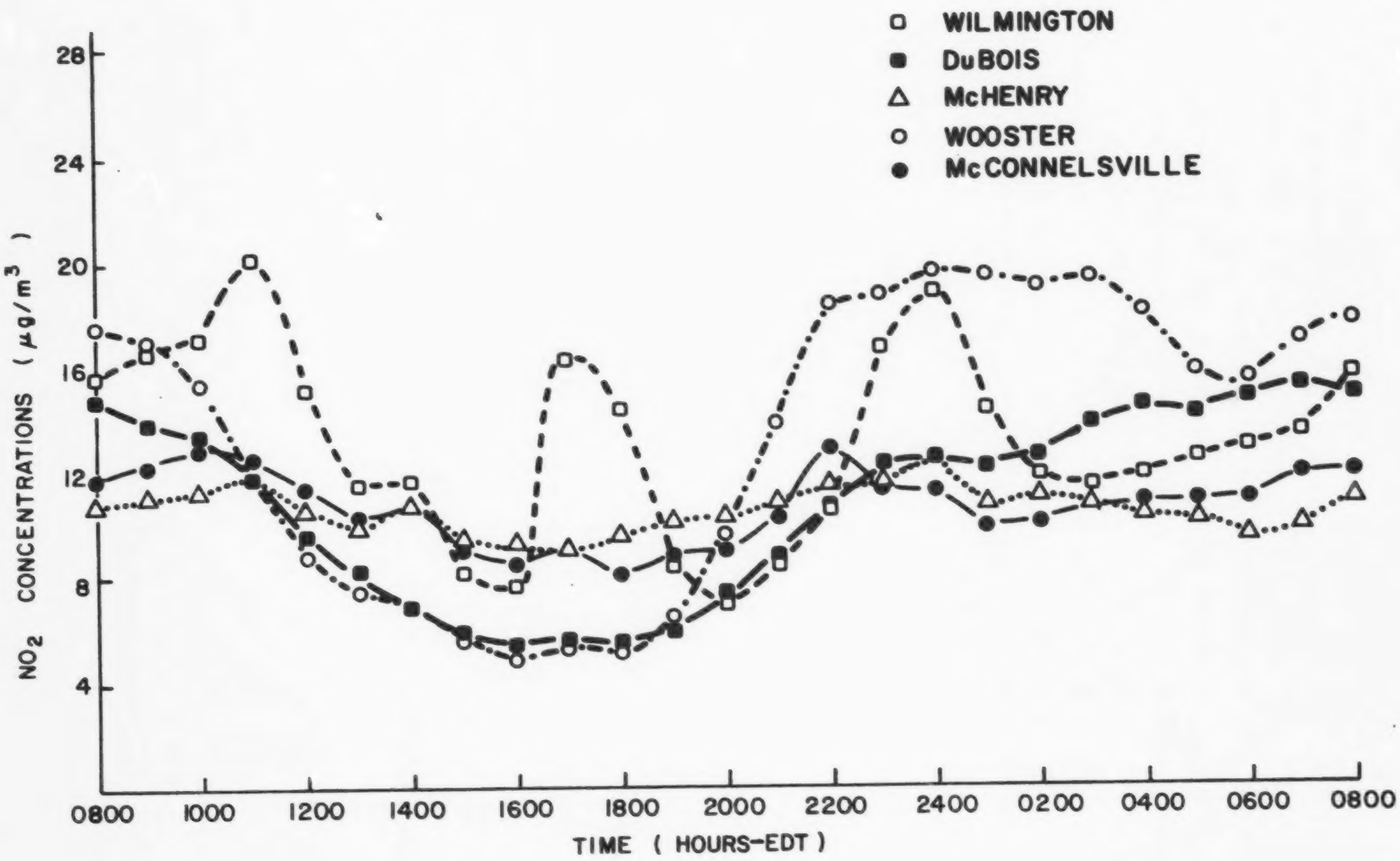


Figure 36. Mean Diurnal Nitrogen Dioxide Concentrations at Wilmington, Wooster, McConnelsville, Ohio; DuBois, Pennsylvania; and McHenry, Maryland from June 14-August 31, 1974.

figures 37-39. The shaded area between the total hydrocarbon and methane curves represents the mean hourly nonmethane hydrocarbon concentration, as determined by subtracting the CH_4 measurement from the THC measurement of the Beckman 6800 THC, CH_4, CO analyzer.

Mean hourly nitrogen dioxide concentrations from all five rural stations ranged from approximately 5-25 $\mu g/m^3$. A majority of these measurements were at or below the generally accepted minimum detectable level of 10 $\mu g/m^3$ for the measurement method. Mean hourly total hydrocarbon and methane measurements at two stations in Ohio did not exhibit much variability or diurnal pattern (i.e., Wilmington and McConnelsville). A diurnal variation was apparent at Wooster. Nonmethane hydrocarbon ($THC-CH_4$) concentrations were low ($> 80\ \mu g/m^3$) at Wilmington and higher at McConnelsville and Wooster (i.e., 100-230 $\mu g/m^3$). A consistent diurnal pattern was not evident. Carbon monoxide concentrations were variable at Wilmington, ranging from a low of 270 to a high of 500 $\mu g/m^3$, peaked at 1700 at Wooster, and were uniformly consistent at McConnelsville. These concentration values are higher at all stations than the geochemical background, which is considered to be on the order of 80-140 $\mu g/m^3$.

5.3 Summary of Climatic Conditions

During the last 2 weeks of June, temperatures over the study area averaged 6 degrees below normal with a cold period during the last week (6-8°F below normal). Precipitation, a total of 5.08-7.62 cm, occurred during the last week, as a broad low-pressure trough covered the whole area. The resultant wind vectors at 915 m for this period at Dayton, Pittsburgh, and Huntington also indicate the cyclonic curvature associated with the trough aloft (table 15).

July of 1974 was unusually dry. Dayton, Ohio, received only 14 percent of its normal monthly rainfall of 8.99 cm. Throughout the study area, precipitation ranged from 2.54-7.62 cm below normal for the month. Sunshine was relatively abundant, ~65 percent of maximum possible for the month. Mean monthly temperature departures from the 30-year mean of -1°F to +1°F were recorded, which is well within normal variability. The resultant winds at 915 m were predominantly westerly with lower speeds (~2.8 m/sec) than

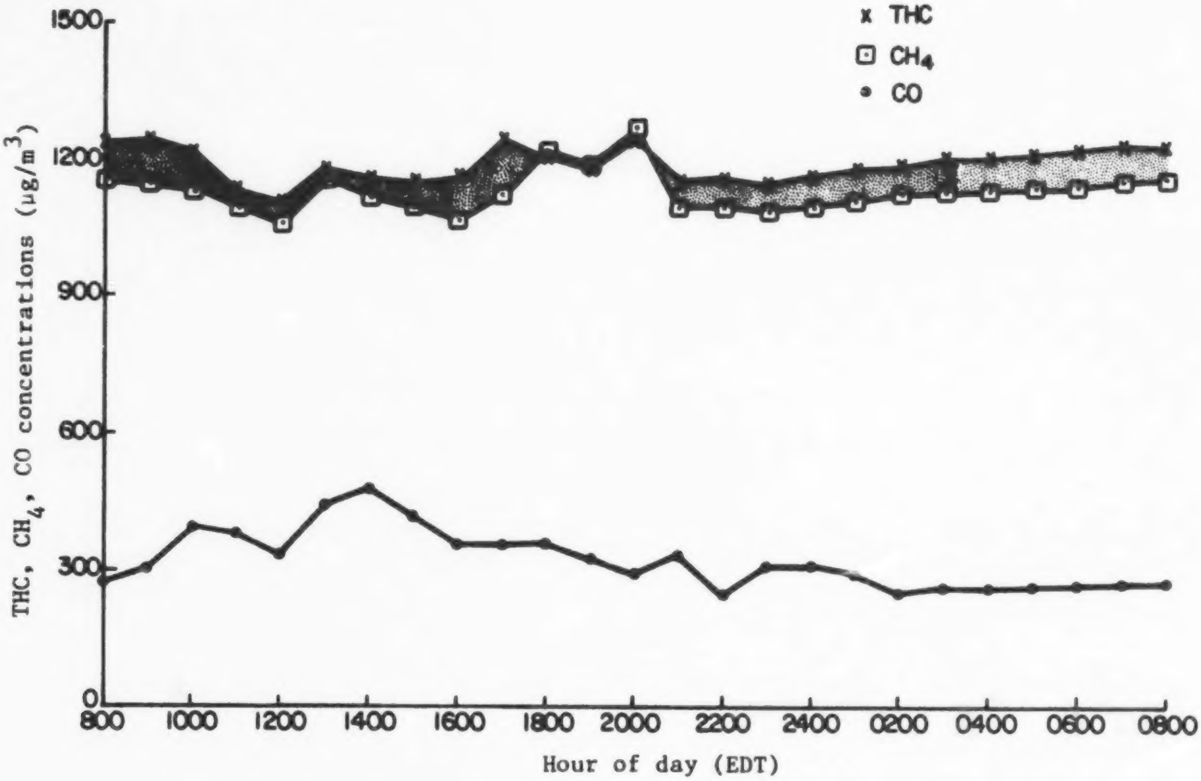


Figure 37. Mean diurnal concentration of total hydrocarbon, methane, and carbon monoxide for Wilmington, Ohio, from June 14-August 31, 1974.

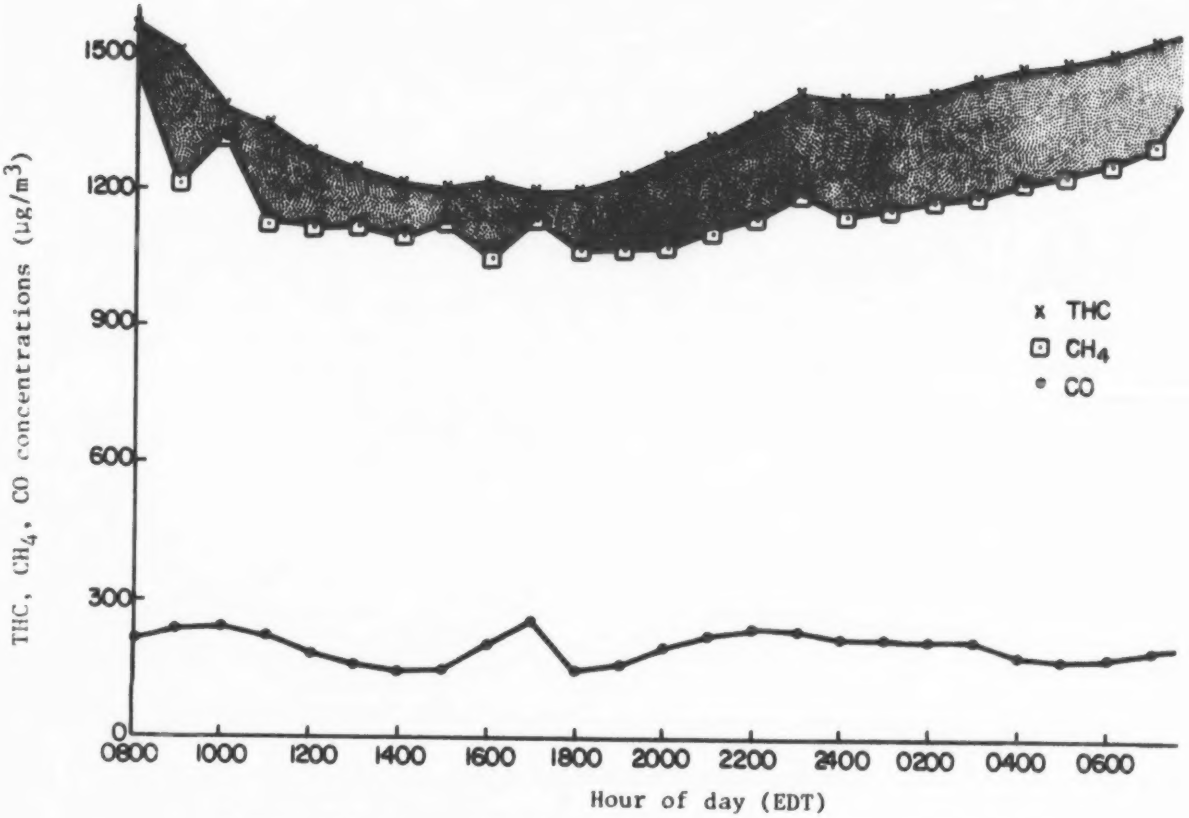


Figure 38. Mean diurnal concentration of total hydrocarbon, methane, and carbon monoxide for Wooster, Ohio, from June 14-August 31, 1974.

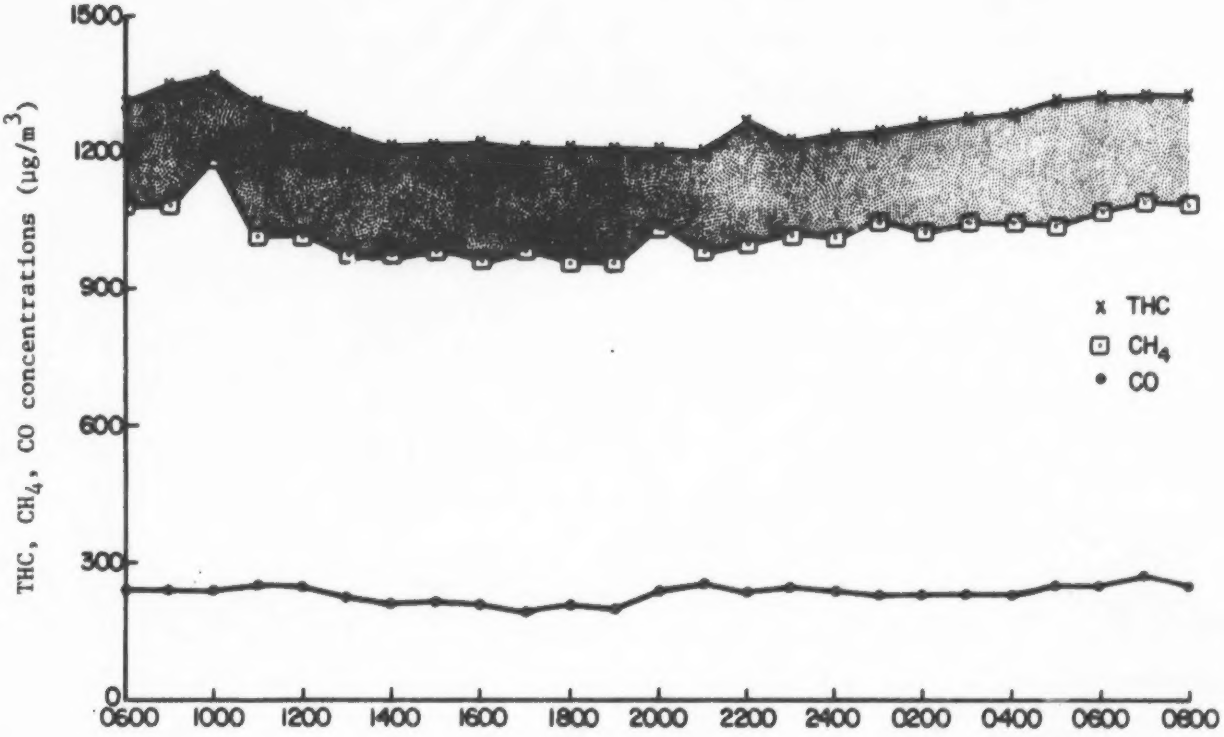


Figure 39. Mean diurnal concentration of total hydrocarbon, methane, and carbon monoxide for McConnelsville, Ohio, from June 14-August 31, 1974.

Table 15. Comparison of low-altitude resultant wind velocity at selected locations by months

Month	Year	Location		
		Pittsburgh	Dayton	Huntington
June	1974*	233/3.1**	288/2.5	249/4.9
	1973	260/6.3	250/6.9	250/5.7
	1972	280/6.3	290/5.0	280/5.0
July	1974*	284/3.3	265/2.5	276/2.7
	1973	270/4.7	280/3.7	280/4.6
	1972	270/4.3	270/4.9	270/4.6
August	1974*	207/3.7	241/3.0	235/2.8
	1973	280/3.3	280/2.9	280/2.9
	1972	260/4.2	270/4.3	280/5.4

*The 1974 data computed from incomplete sets of teletype reports of the 915 meters wind vector. The 1972 and 1973 data are taken from Climatological Data, National Summary, for the 900 mb surface (~1,050 m).

**Wind direction (deg)/wind speed (m/sec).

in the previous 2 years. This suggests that low-pressure systems passed north of the area, moving primarily west to east. The monthly mean 700 mb (~ 3 km) charts substantiate that type of flow.

In August, precipitation returned to the area, with 1.5 times normal monthly rainfall at most stations. Resultant winds at Pittsburgh at 915 m showed a major shift toward southerly flow. Surface weather maps suggest high pressure was common along the eastern seaboard, giving a flow of air into the study area from the east. The air flow at 500 mb shows a persistent long wave trough which slowly regressed across the area, but with frequent, minor disturbances moving through. Potential temperature time sections from the ground to 5 km, at Dayton and at Pittsburgh show no major disturbances in the vertical structure of the atmosphere during August.

In general, departures from long-term averages for various climatic variables occurred in one portion of the study period and were compensated for in other portions. Over the period, the weather conditions approximated a "normal" summer.

6.0 EXAMINATION AND INTERPRETATION OF RESULTS

The data obtained during this study can be divided into three sections: measurements at rural ground stations, data from six suburban locations, and data from aircraft flights. Results obtained in each of these areas have been analyzed both as individual sets and in relation to each other. An attempt has been made to develop a comprehensive pattern of relationship between ozone concentrations over rural areas and urban sources of ozone precursors. In reviewing the analyses that follow, one must keep in mind that the "parcel" of air which has been sampled does not represent a closed system. That particular parcel has had a unique history involving injection of contaminants from anthropogenic and natural sources at unknown rates and quantities, and mixing with adjacent parcels, each having its own unique history. Throughout the life of the parcel, reactions producing and destroying ozone are continually in progress. Each concentration measurement made during this study involved some averaging in time, space, or both. As a consequence, extreme variations in concentrations adjacent in time or space, for the most part, are eliminated. However, since the distribution of contaminant concentrations is not likely to be smooth function, there was the possibility of sampling a uniquely high or low concentration.

6.1 Examination and Interpretation of Ozone and Hydrocarbon Data from Aircraft Flights

The rationale for the two types of survey flights, square wave and double box patterns, is given in section 2. The square wave pattern was flown on a clear day when orderly wind speed and wind direction were predicted to last for a period of hours. The pattern was flown starting upwind and continuing downwind of Columbus. On days of disorganized, low wind speed and stagnant conditions, the double box pattern was flown around the airspace of Columbus.

In order to aid in the understanding of the discussion of the airborne studies, an outline of the flight patterns and a discussion of their features is given below.

Figure 40 illustrates the square wave pattern. In this example, the wind at flight altitude is from the east. The plane departs from the base station at Wilmington and flies to a point upwind (i.e., to the east) of Columbus. The plane enters the flight pattern by flying the first crosswind "leg;" spoken of as "leg-1" in the discussion. Additional crosswind flights are spoken of as "leg-2," "leg-3," etc.

Figure 41 illustrates the double box pattern. This type of flight always originated at the Wilmington base station. After a portion of the diagonal towards the northeast is flown, the inner box of the pattern is traversed. The sides of the inner and outer box are considered as flight legs and numbered sequentially counterclockwise with the northern side of the inner box assigned as leg 1, the western side of the inner box as leg 2, etc., and the northern side of the outer box as leg 5, the western side of the outer box as leg 6, etc.

Individual ozone readings and areas where hydrocarbon bag samples are collected are entered on drawings of the flight patterns. It is suggested that frequent reference be made to these drawings while one reads the discussion and interpretation of aircraft data.

Various flight conditions and meteorological summaries are given in appendix C. Concentrations of ground station's pollutants are summarized in tables and graphs in section 5 and in full form in the computer printouts which were supplied to the project monitor.

The rationale for choosing the data (primary and derived) given in tables in this section were the following. Ozone was presented for comparison with hydrocarbon data. Acetylene was chosen as a key compound in the interpretation of the hydrocarbon data because it is recognized as the best index compound for exhaust from the internal combustion engine. As far as is known, acetylene has no natural sources. Furthermore, acetylene is one of the most inert of all hydrocarbons in an atmospheric photochemical system. Very little is known about the relative abundance of other hydrocarbons in nature, and one cannot, from an examination of the literature, choose with much certainty a compound other than acetylene as an index of anthropogenic hydrocarbon emissions. Even butane and alkylated benzenes have natural origins in vegetation and soil and would be expected in natural crude-oil seepage. Since acetylene does not react appreciably on the time scale

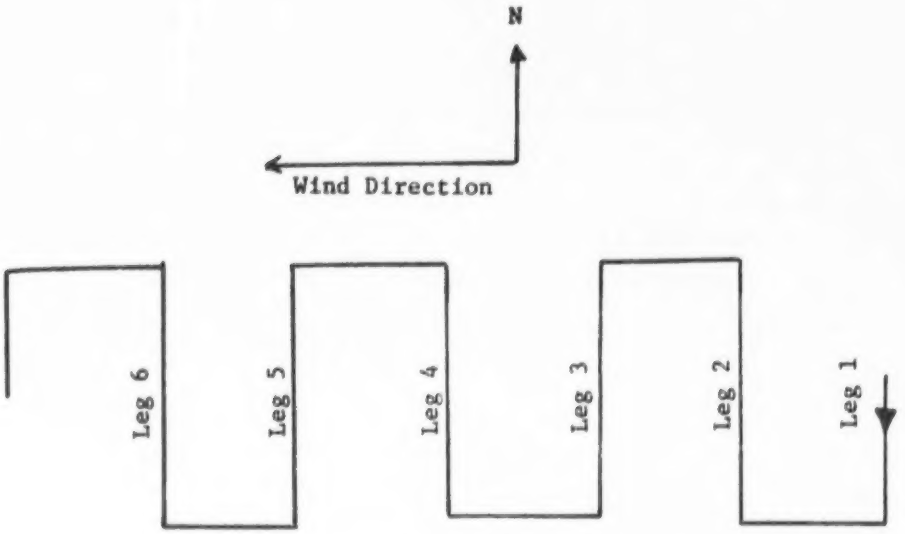

N
Wind Direction
Leg 6
Leg 5
Leg 4
Leg 3
Leg 2
Leg 1

Figure 40. Square wave flight pattern.

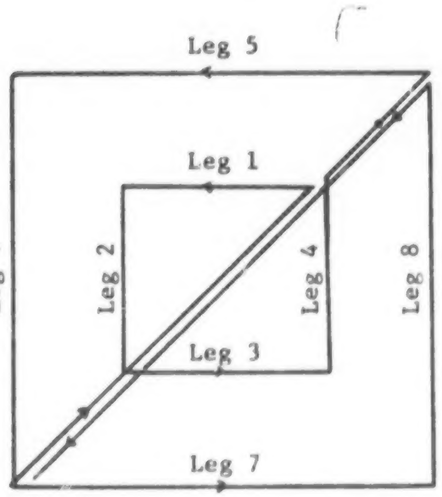

Leg 5
Leg 1
Leg 6
Leg 2
Leg 4
Leg 8
Leg 3
Leg 7

Figure 41. Double box flight pattern.

involved, other substances were compared to it to separate decreases caused by dilution from the changes caused by chemical reaction.

The measured concentrations presented for acetylene and other hydrocarbons were in the parts per billion (as carbon) range, and it is recognized that there is a real problem in analysis at these concentrations. At such low concentration, a small absolute error can result in a very large relative error. Although any given value may be in error, it is felt that the analyses taken as a whole furnish an emerging picture of the process of ozone generation in rural air.

Although not much is known on natural sources for acetaldehyde, the acetaldehyde/acetylene ratio was computed and tabulated. In a smog system, acetaldehyde should be generated more rapidly than it is destroyed.

Carbon monoxide, like acetylene, should not react appreciably on the time scales involved. Since CO is generated by all combustion sources and acetylene only by oxidation and cracking in the automobile engine, a comparison of the two should be informative. It should be kept in mind that CO also has natural sources. Isobutylene/isobutane and propylene/propane ratios were expected to provide an index of the degree of reaction the hydrocarbons had undergone in the ozone-generative processes. Ethylbenzene was chosen to be compared with acetylene because it is a representative aromatic compound and is less likely to be a sample contaminant than toluene or benzene. The propylene/acetylene ratio was also chosen to be an index of oxidation by ozone and photochemical processes.

6.1.1 Square Wave Flights

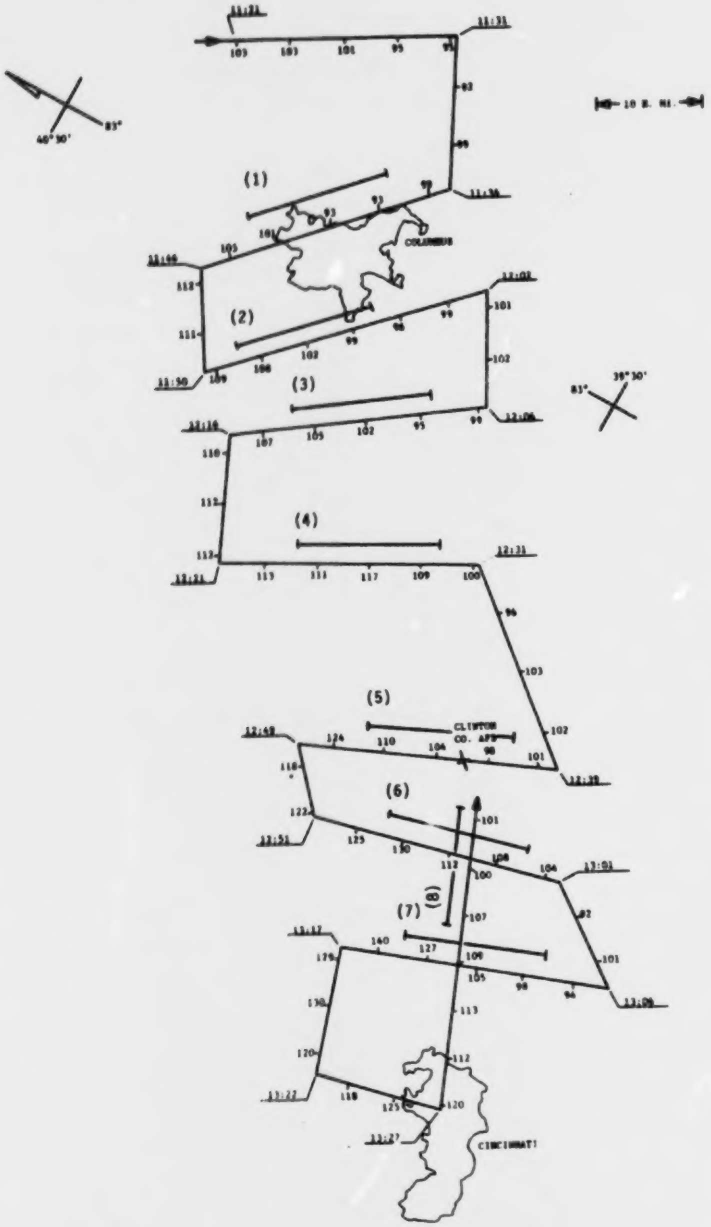
Five separate square wave patterns were flown during the course of this study. Four of these are examined in detail below.

1. Square Wave Flight of Saturday, June 27, 1974

This flight began upwind of Columbus and continued to Cincinnati. The somewhat irregular flight path is shown in figure 42. Hydrocarbon data and ratios are given in table 16.

Diurnal Variation of Ozone Concentration

There is little apparent diurnal ozone change at flight level. The average ozone concentration for the first crosswind leg was 101 $\mu g/m^3$; for the last crosswind leg, 113 $\mu g/m^3$.


11:21
11:31
11:36
11:46
11:50
12:02
12:06
12:16
12:21
12:31
12:39
12:49
12:51
13:01
13:06
13:17
13:22
13:27
(1)
(2)
(3)
(4)
(5)
(6)
(7)
(8)
COLUMBUS
CLINTON CO. AFB
CINCINNATI
10 N. MI.
40°30'
83°
39°30'

FLIGHT DATE: June 27, 1974

TRUE AIRSPEED: 277.8 km/h (150 knots)

PATTERN. Square Wave

MISSION ALTITUDE: 762.0 m (2,500 ft) above msl

LOW LEVEL WINDS:

Sfc	070°/5.14 m/s (10 knots)
609 m (2,000')	080°/8.74 m/s (17 knots)
914 m (3,000')	065°/8.23 m/s (16 knots)
1219 m (4,000')	055°/7.72 m/s (15 knots)

DATA: Ozone Concentration in $\mu g/m^3$
Time in EDT

Hydrocarbon Sample Positions Denoted by ├────┤ .

Low Level Winds Obtained From National Weather Service
Upper Air Station
Dayton, Ohio-0800 EDT

Figure 42. Square wave flight of June 27, 1974.

Table 16. Abstract of hydrocarbon data: Square wave flight of June 27, 1974.

Category	Sample number (Time of sample collections-EDT)			
	1 (1139)	2 (1153)	3 (1209)	4 (1224)
Ozone, $\mu g/m^3$	96.	103.	101.	112.
Acetylene, ppbc	1.4	2.5	2.3	1.8
Acetaldehyde/acetylene	4.7	1.2	2.6	4.9
Carbon monoxide, ppm	0.27	0.28	0.32	0.27
Carbon monoxide/acetylene	193.	112.	139.	150.
Isobutylene/isobutane	0.5	0.3	0.2	0.2
Propylene/propane	0.2	0.1	0.1	0.2
Ethylbenzene/acetylene	0.4	0.5	0.6	0.8
Propylene/acetylene	0.9	0.3	0.4	0.5

	5 (1242)	6 (1255)	7 (1309)	8 (1335)
Ozone, $\mu g/m^3$	104.	117.	110.	103.
Acetylene, ppbc	1.7	2.5	2.1	1.1
Acetaldehyde/acetylene	3.9	1.8	2.5	6.9
Carbon monoxide, ppm	0.26	0.25	0.32	0.24
Carbon monoxide/acetylene	153.	100.	152.	218.
Isobutylene/isobutane	0.4	0.3	0.3	0.2
Propylene/propane	0.2	0.2	0.2	0.1
Ethylbenzene/acetylene	0.8	0.7	0.2	0.3
Propylene/acetylene	0.5	0.3	0.4	0.5

Variation of Ozone Concentrations Upwind, Over, Downwind of the City

Average ozone concentrations for the eight, crosswind legs of the flight were 99, 98, 102, 102, 110, 107, 116, and 113 $\mu g/m^3$. The ozone variation from the first through the fourth crosswind legs was slight. About 56 km (50 nm) downwind of the center of Columbus, on the fifth crosswind leg, there was a noticeable increase in average ozone concentration. This could indicate a necessary incubation time for occurrence of maximized ozone formation in that parcel of air. An estimate of the time of origin of that air parcel from the center of Columbus was computed as follows. If a constant wind speed of 8 m/sec (15 knots) is assumed, approximately two hours would have passed since the air now in the area of leg 5 left the center of Columbus. Subtracting two hours from the time of collection, 1224, gives 1024 as the estimated of the time the air parcel was over Columbus. In the seventh leg, the average ozone concentration increased to 116 $\mu g/m^3$ in air parcel, which was estimated to have left the center of Columbus around 0900. That time may well have corresponded to the time of increased human activity in Columbus on this Saturday morning. Air in that parcel would be expected to contain higher concentrations of city-emitted hydrocarbons than adjacent samples, and, in fact, it did.

Other Ozone Variations

In figure 42, there appears to be a gradient in ozone concentration (from higher to lower) crosswind from east to west. The average ozone concentration on the western side of the pattern is 119 $\mu g/m^3$; on the eastern side, 100 $\mu g/m^3$. The presence of this gradient was due, in part to the higher ozone concentrations, up to 140 $\mu g/m^3$, observed west of Wilmington and northeast of Cincinnati. Several other ozone concentrations depict a hot spot of ozone in that vicinity and suggest the presence of an urban plume; however, no specific source for the plume can be deduced from the available data.

Variation of Hydrocarbon Concentrations and Ratios

Concentrations of two hydrocarbons versus distance from the city are shown in figure 43. The figure shows the presence of hydrocarbons from the city in samples one, two, and three. Two miles upwind of the city center (sample one) both acetylene and isopentane concentrations were lower

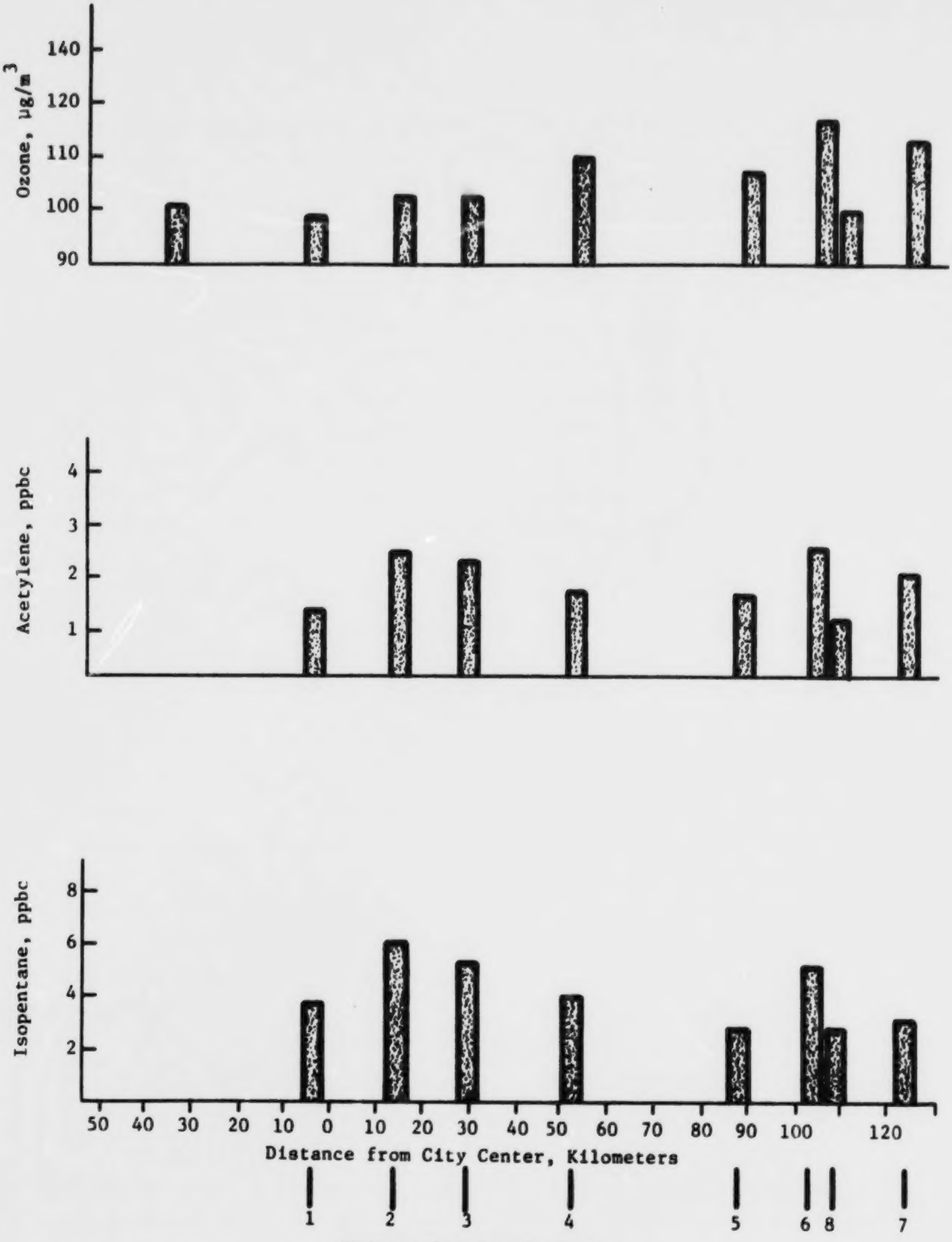


Figure 43. Ozone, acetylene, and isopentane concentrations upwind and downwind of Columbus. Flight of June 27, 1974.

than they were in samples two and three which were collected immediately downwind of the city. That ozone concentration does not increase noticeably immediately downwind of the city can be explained in two ways. (1) The concentration of ozone entering the city from upwind is initially depressed or quenched by nitric oxide and other ozone-reactive compounds being emitted from the city. (2) Due to the city's influence on the chemical composition of the air mass, a certain induction period is required for ozone formation to again "peak," thus an increase is observed at a later time, that is, further downwind. This time period would be dependent on solar irradiation and movement of the air.

The hydrocarbon concentration (as shown by acetylene and isopentane) began to fall off in the samples taken on the fourth, fifth, and sixth legs. But on the seventh leg, the concentration of both acetylene and isopentane increased. This rise was more or less coincident with the increase in ozone, showing a relationship between ozone, hydrocarbons, the time of the air parcel's emission from the city (e.g., in the morning during presumed maximum human activity), and distance from the city.

The data show a preexisting level of both ozone and hydrocarbons upwind of the city. Of course, injection of ozone-precursor materials from both natural and anthropogenic sources into the air before it entered the city was constantly occurring.

Comparison of Aircraft Data with Ground-Station Data

The ground station at Wilmington, Ohio, was directly below the line of flight followed on June 27, 1974. The parcel of air that gave the enhanced ozone and hydrocarbon readings on the seventh leg of the flight is estimated to have been near Wilmington around 40 minutes earlier, that is 1215 EDT. On the ground, the ozone concentration was very constant from 1000 until 1200, increasing only 2 $\mu g/m^3$ (from 76 to 78 $\mu g/m^3$). In the internal 1200-1215, the ozone concentration rose by 12 $\mu g/m^3$ to 89 $\mu g/m^3$. Ozone concentration continued to increase and peaked at a concentration of 143 $\mu g/m^3$ at 1645. It is tenuous, however, to associate the 12-$\mu g/m^3$ rise in ozone concentration with the passage of the high hydrocarbon-content air parcel over Wilmington. The hydrocarbon-carbon monoxide analyzer was off-line at Wilmington on this day so no comparison of these pollutants could be made with the aircraft data.

At the ground station in Columbus, the ozone concentration was approximately 4 $\mu g/m^3$ for the hour ending at 0500. The hourly average from 1100 to 1200 was missing from the data. The peak hourly average concentration for the day was 157 $\mu g/m^3$ for the period 1800-1900.

2. Square Wave Flight of Tuesday, July 16, 1974

The orientation of the transport wind during this flight gave another opportunity to examine the possibility of one city's influence upon the ozone concentration of another. Ozone concentrations at several Ohio ground stations on July 16 were low when compared to those of other July days. The flight track is shown in figure 44. Hydrocarbon data are summarized in table 17.

Diurnal Variation of Ozone Concentration

To assess the concentration trend with time, data along the straight, return flight path were compared with data from approximately the same space along the flight legs of the square wave pattern. Thus, in the portion of the flight path over Dayton only the value along the return flight leg, 189 $\mu g/m^3$, was compared with the value 188 $\mu g/m^3$, measured on the crosswind leg of the square wave. At the next intersection of flight paths, 177 $\mu g/m^3$ was compared to an earlier 156 $\mu g/m^3$, and so forth. A statistical test applied to these two data sets showed that one was not significantly different from the other. There was, however, a slight tendency toward higher concentrations with the passage of time.

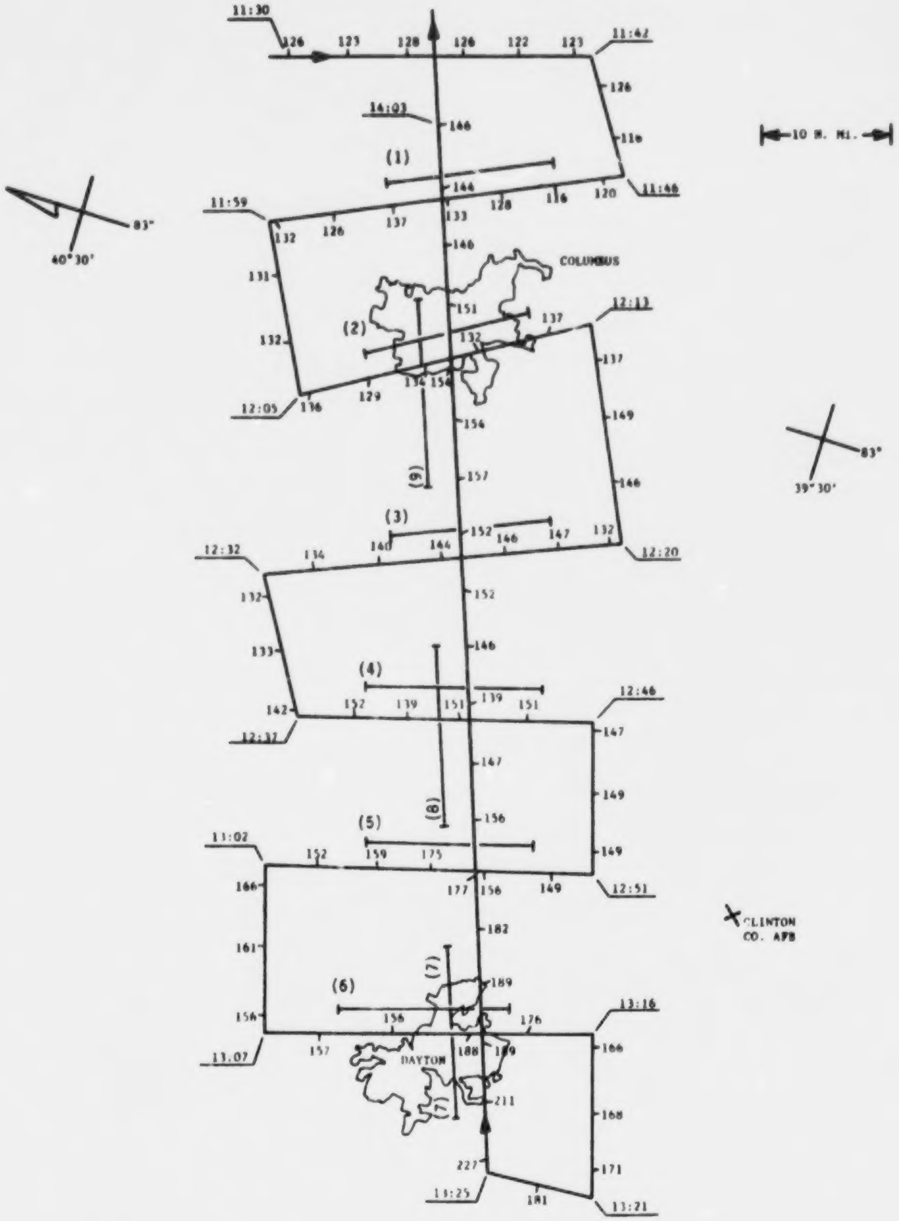
Variation of Ozone Concentrations Upwind, Over, and Downwind of the City

The data were next statistically examined for trends with distance and time from the Columbus urban area. For this analysis data from each "tooth" of the square wave was considered as a data set. (A "tooth" consists of one downwind leg and two crosswind legs.) Each set contains data points common with the preceding set. However, when tested at the 0.05 level, data of the first set were found to be significantly different from the other sets.

Average values for each data set are plotted versus distance from the center of Columbus in figure 45. These indicate a consistent increase in ozone downwind of the city.

Other Ozone Variations

Differences in ozone concentrations north and south of the center


11:30
126
123
128
126
122
123
11:42
126
116
11:46
14:03
146
(1)
144
133
128
116
120
11:59
132
126
137
146
COLUMBUS
131
151
(2)
132
137
12:13
137
132
134
154
129
12:05
136
154
149
(9)
157
146
(3)
140
144
152
146
147
132
12:20
12:32
134
132
152
133
146
(4)
142
152
139
151
139
151
12:46
12:37
147
147
149
(8)
156
(5)
13:02
152
159
175
149
166
177
156
149
12:51
182
161
(7)
189
(6)
156
156
176
13:16
13:07
157
DAYTON
188
189
166
(7)
211
168
227
171
13:25
181
13:21
10 N. Mi.
40°30'
83°
39°30'
83°
CLINTON
CO. AFB

FLIGHT DATE: July 16, 1974

TRUE AIRSPEED: 250.0 km/h (135 knots)

PATTERN: Square Wave

MISSION ALTITUDE: 914.4 m (3,000 ft) above msl

LOW LEVEL WINDS:	
Sfc	060°/1.54 m/s (3 knots)
609 m (2,000')	080°/5.14 m/s (10 knots)
914 m (3,000')	060°/3.60 m/s (7 knots)
1219 m (4,000')	015°/4.12 m/s (8 knots)

DATA: Ozone Concentration in μg/m³
Time in EDT

Hydrocarbon Sample Positions
Denoted by ├────┤.

Low Level Winds Obtained From
National Weather Service
Upper Air Station
Dayton, Ohio-0800 EDT

Figure 44. Square wave flight of July 16, 1974.

Table 17. Abstract of hydrocarbon data: Square wave flight of July 16, 1974

Category	Sample number (time of sample collection-EDT)								
	1 (1149)	2 (1207)	3 (1222)	4 (1254)	5 (1254)	6 (1310)	7 (1327)	8 (1337)	9 (1349)
Ozone, $\mu g/m^3$	133	134	145	148	175	188	189	145	155
Acetylene, ppbc	2.1	2.9	1.7	1.8	---	3.1	3.5	1.9	1.4
Acetaldehyde/acetylene	2.8	1.9	7.1	3.1	---	1.7	2.1	2.2	3.9
Carbon monoxide, ppm	0.28	0.36	0.30	0.34	0.40	0.44	0.45	0.28	0.24
Carbon monoxide/acetylene	133.	124.	177.	189.	---	142.	129.	147.	171.
Isobutylene/isobutane	0.5	0.4	0.4	0.3	0.3	0.3	0.4	0.4	0.6
Propylene/propane	0.2	0.2	0.1	0.2	---	0.3	0.4	0.2	0.2
Ethylbenzene/acetylene	0.4	0.3	0.3	0.8	---	0.2	0.3	0.3	7.7
Propylene/acetylene	1.2	0.7	0.4	0.6	---	0.6	0.7	0.8	0.6

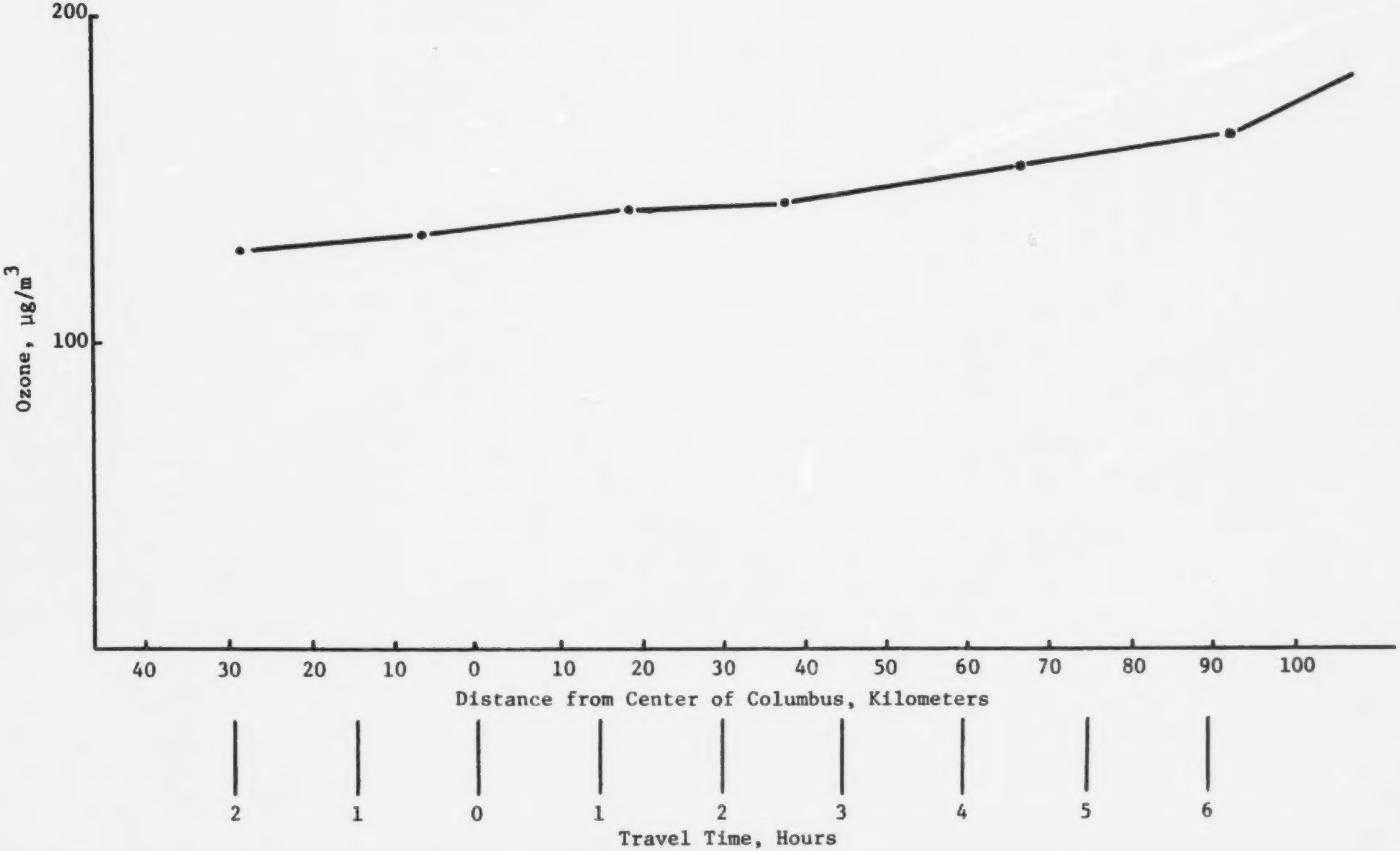


Figure 45. Ozone concentration versus distance and time along the line of wind flow. Flight of July 16, 1974.

line of the flight were small. Center line concentrations upwind and up to about 40 km downwind of the city were higher than along the corresponding edges, but then decreased slightly further downwind. Nearer, but upwind of Dayton, the centerline concentrations increased more rapidly than the edge concentrations.

Variation of Hydrocarbon Concentrations and Ratios

Hydrocarbon samples 2, 6, 7, and 9 were taken over the urban areas of Columbus and Dayton. Except for a sample 9, the samples collected over urban areas had a higher acetylene concentration than those collected over "rural" areas.

When concentrations of the gases isopentane, acetylene, and carbon monoxide are plotted versus distance from the center of Columbus (figure 46), in each case the concentration in sample 2 was higher than in sample 1. With increasing distance from the city, the concentrations gradually decreased until, about 56 km (30 nm) downwind, the concentrations approached those observed in the air 19 km (10 nm) upwind of Columbus. The fifth sample (taken on crosswind leg 6) has an elevated value of isopentane and carbon monoxide. The acetylene concentration is missing due to analytical problems. If the wind direction and speed stayed constant at 073° and 3.6 m/sec (7 knots), the parcel of air at leg 6 would have been in the Columbus metropolitan area around 0646. This roughly corresponds to the time of early morning traffic buildup, and so these elevated hydrocarbon concentrations downwind could be due to this Tuesday morning traffic.

Hydrocarbon samples 6 and 7 were taken over the Dayton area and contain the highest acetylene concentrations observed. The ozone concentrations at Dayton were also the highest observed. Since the acetylene concentration over Dayton was almost twice the value of sample 4 (whose concentration is assumed to be due in part to Columbus), it seems that Dayton's higher acetylene concentration (over that of sample 4) was due to emissions in and near Dayton itself.

Comparison of Aircraft Data with Ground Station Data

The overall ozone concentration measured aloft during the flight was higher than that reported by any of the ground stations of Cincinnati, Dayton, Columbus, or Wilmington.

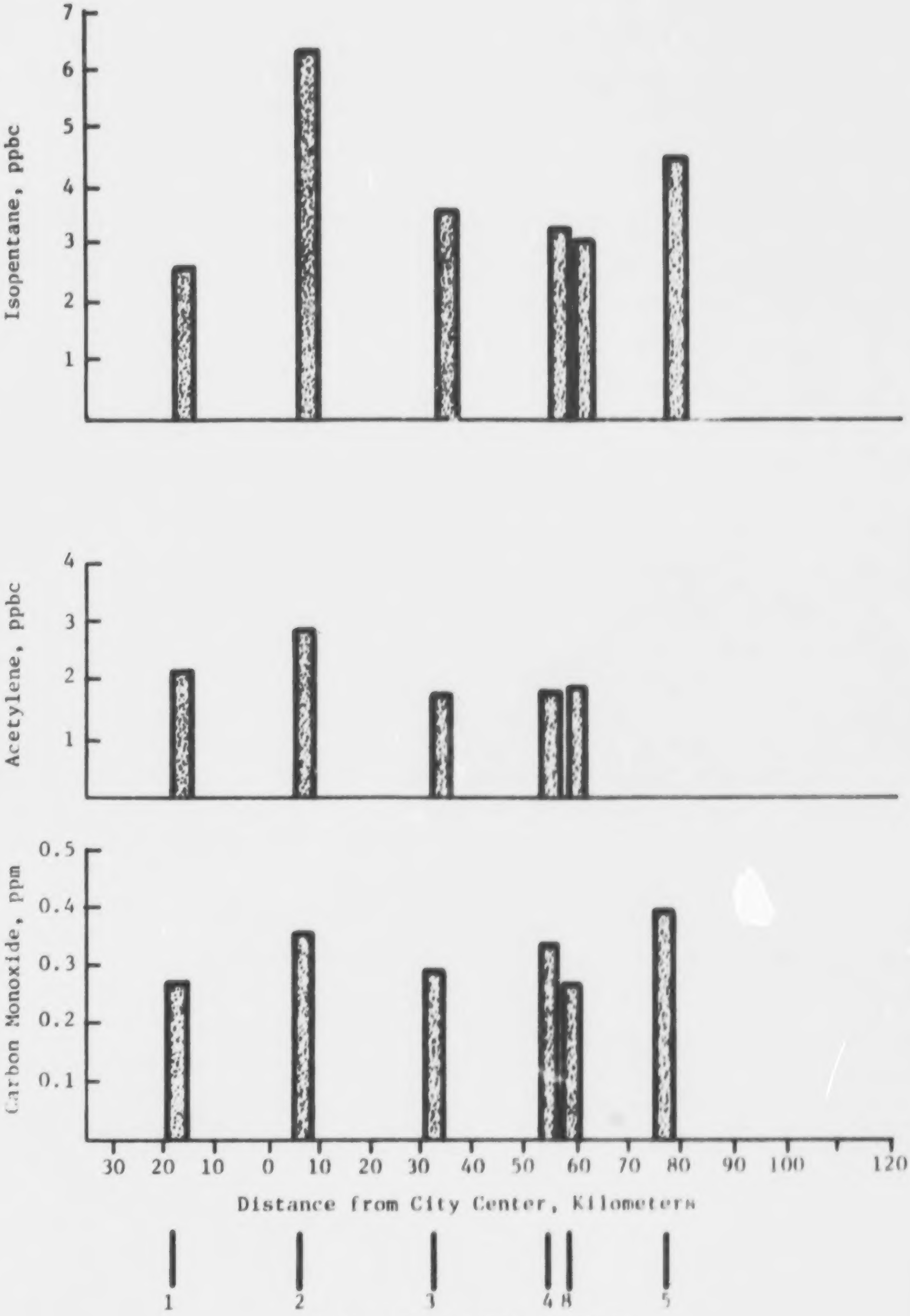


Figure 46. Isopentane, acetylene, and carbon monoxide concentrations upwind and downwind of Columbus. Flight of July 16, 1974.

3. Square Wave Flight of Sunday, July 21, 1974

This was the only square wave flight made on a Sunday. During the flight, ground level ozone concentrations in Columbus were less than 140 $\mu g/m^3$ all day. Ozone concentrations at Wilmington were about 110 $\mu g/m^3$ at 1200 but increased to over 160 $\mu g/m^3$ by 1400 and exceeded 200 $\mu g/m^3$ at 1800 EDT. Ozone concentrations at rural locations in Ohio showed similar behavior. The flight track is shown in figure 47. Hydrocarbon data are summarized in table 18.

Diurnal Variation of Ozone Concentration

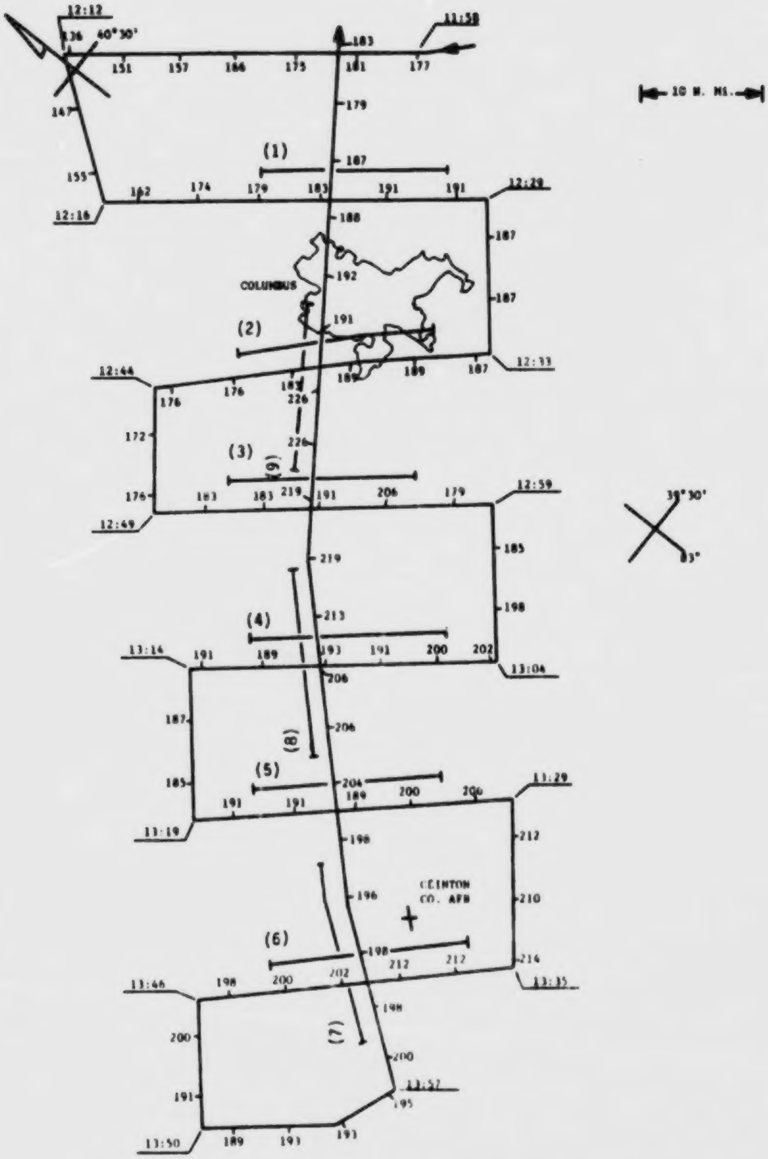
Comparison of ozone concentrations near intersecting points of the flight path shows that there was little diurnal variation at points over "rural" areas. However, at the point of intersection just downwind of the city, an increase of 40 $\mu g/m^3$ ozone was noted during a 2-hour time period.

Variation of Ozone Concentrations Upwind, Over, and Downwind of the City

The average ozone concentration increased for each successive crosswind leg downwind of Columbus. Ozone values recorded on the outer edges of the flight pattern also showed a steady increase with both time and increasing distance downwind of the city.

Variation of Hydrocarbon Concentrations and Ratios

When the concentrations for the gases, acetylene, isopentane, and carbon monoxide are plotted in figure 48 versus distance from the city for samples 1, 2, 3, 4, 5, and 6 (crosswind legs 2, 3, 4, 5, 6, and 7, respectively), a definite increase in concentration of each was noted as the plane flew into the Columbus area. Then, as samples were collected farther and farther downwind, steadily lower concentrations were observed. No "bulge" in hydrocarbon concentrations occurred downwind, as was seen in other square wave flights. It should be noted that this flight occurred on Sunday, a day without typical workday traffic patterns. Beyond about 74 km (40 nm) these pollutants were found to be at about the same concentrations as they were upwind of the city.


12:12
136
40°30'
151
157
166
175
181
183
11:58
177
10 N. MI.
147
179
(1)
187
155
162
174
179
183
191
191
12:29
12:16
188
187
COLUMBUS
192
187
191
(2)
12:44
176
176
183
189
189
187
12:33
226
172
226
(3)
(9)
176
183
183
219
191
206
179
12:59
12:49
39°30'
83°
219
185
198
213
(4)
13:14
191
189
193
191
200
202
13:04
206
187
206
(8)
(5)
185
204
189
200
206
13:29
191
191
13:19
198
212
CLINTON
CO. AFB
196
210
(6)
198
212
212
214
13:46
198
200
202
13:35
198
200
(7)
200
191
13:57
195
13:50
189
191
193

FLIGHT DATE: July 21, 1974

PATTERN: Square Wave

TRUE AIRSPEED: 259.3 km/h (140 knots)

MISSION ALTITUDE: 975.36 m (3,200 ft) above msl

LOW LEVEL WINDS:		
	Sfc	030°/3.09 m/s (6 knots)
	609 m (2,000')	060°/6.17 m/s (12 knots)
	914 m (3,000')	055°/4.12 m/s (8 knots)
	1219 m (4,000')	[illegible]/3.60 m/s (7 knots)

DATA: Ozone Concentration in $\mu g/m^3$
Time in EDT
Hydrocarbon Sample Positions
Denoted by ├──────┤.

Low Level Winds Obtained From
National Weather S[illegible]
Upper Air Station
Dayton, Ohio-0800 EDT

Figure 47. Square wave flight of July 21, 1974.

Table 18. Abstract of hydrocarbon data: Square wave flight of July 21, 1974

Catetory	Sample number (time of sample collection-EDT)								
	1 (1222)	2 (1235)	3 (1251)	4 (1306)	5 (1321)	6 (1337)	7 (1359)	8 (1410)	9 (1419)
Ozone, $\mu g/m^3$	180	183	188	194	195	206	197	208	216
Acetylene, ppbc	1.4	2.8	2.2	1.8	1.8	1.4	1.5	1.8	2.8
Acetaldehyde/acetylene	1.6	1.3	1.6	2.8	1.3	1.6	1.9	1.5	1.0
Carbon monoxide, ppm	0.24	0.37	0.30	0.28	0.26	0.23	0.23	0.26	0.33
Carbon monoxide/acetylene	171.	132.	136.	156.	144.	164.	153.	144.	118.
Isobutylene/isobutane	0.3	0.3	0.4	0.6	0.3	0.6	0.3	0.3	0.3
Propylene/propane	0.3	0.4	---	0.6	0.3	0.4	0.3	0.4	0.8
Ethylbenzene/acetylene	0.0	0.1	0.0	0.1	0.1	---	---	0.1	0.2
Propylene/acetylene	0.8	0.5	---	1.3	0.6	0.7	0.5	0.9	1.0

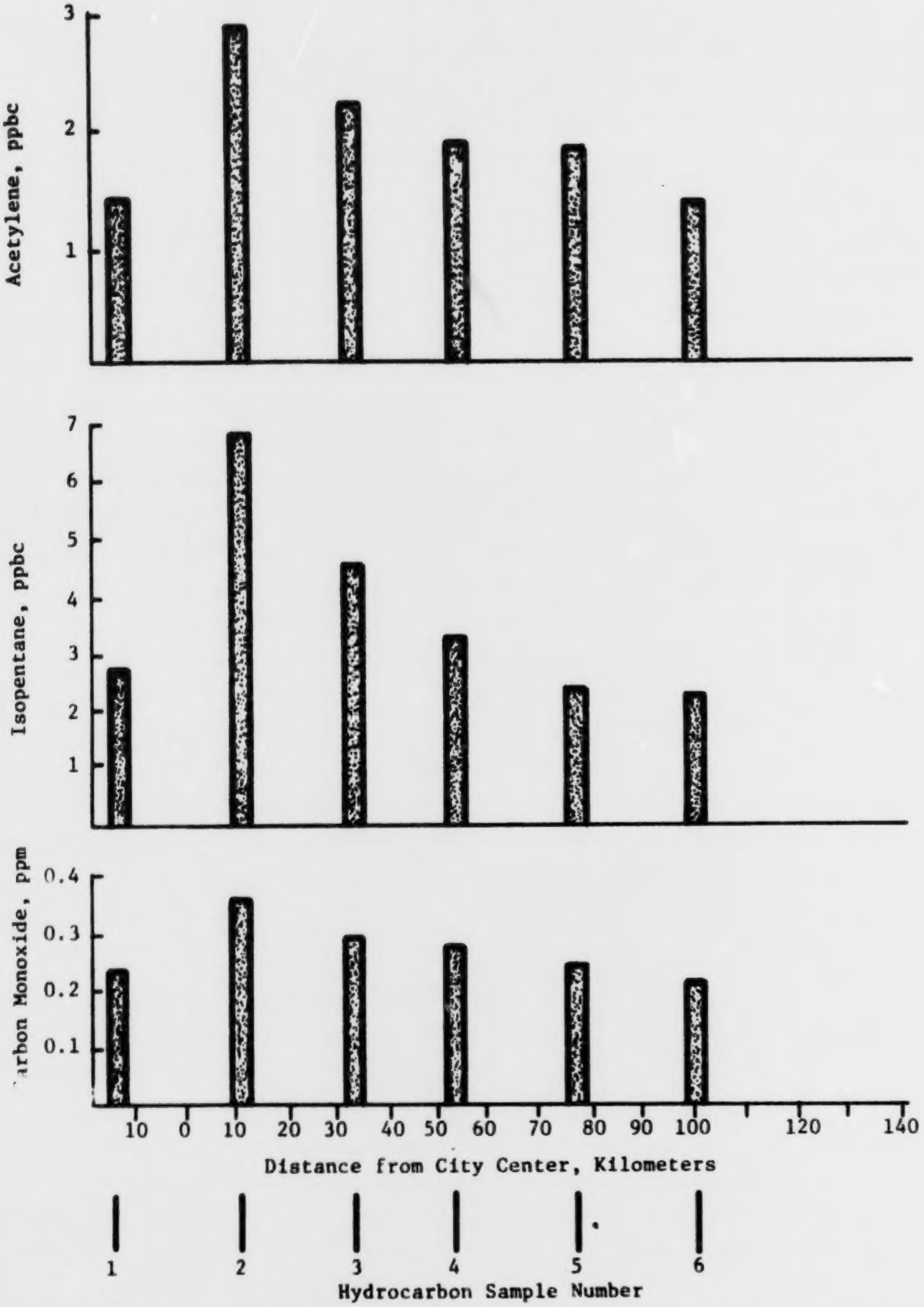


Figure 48. Acetylene, isopentane, and carbon monoxide concentrations upwind and downwind of Columbus. Flight of July 21, 1974.

4. Square Wave Flight of Thursday, July 25, 1974

Navigational difficulties were encountered during this flight. Thus, the flight track is very irregular. The flight track is shown in figure 49. Hydrocarbon concentrations and ratios are given in table 19.

Diurnal Variation of Ozone Concentration

There appeared to be little diurnal variation of ozone based on a comparison of average concentration taken upwind of the city of Columbus at the beginning (185 $\mu g/m^3$) and end of the flight (180 $\mu g/m^3$).

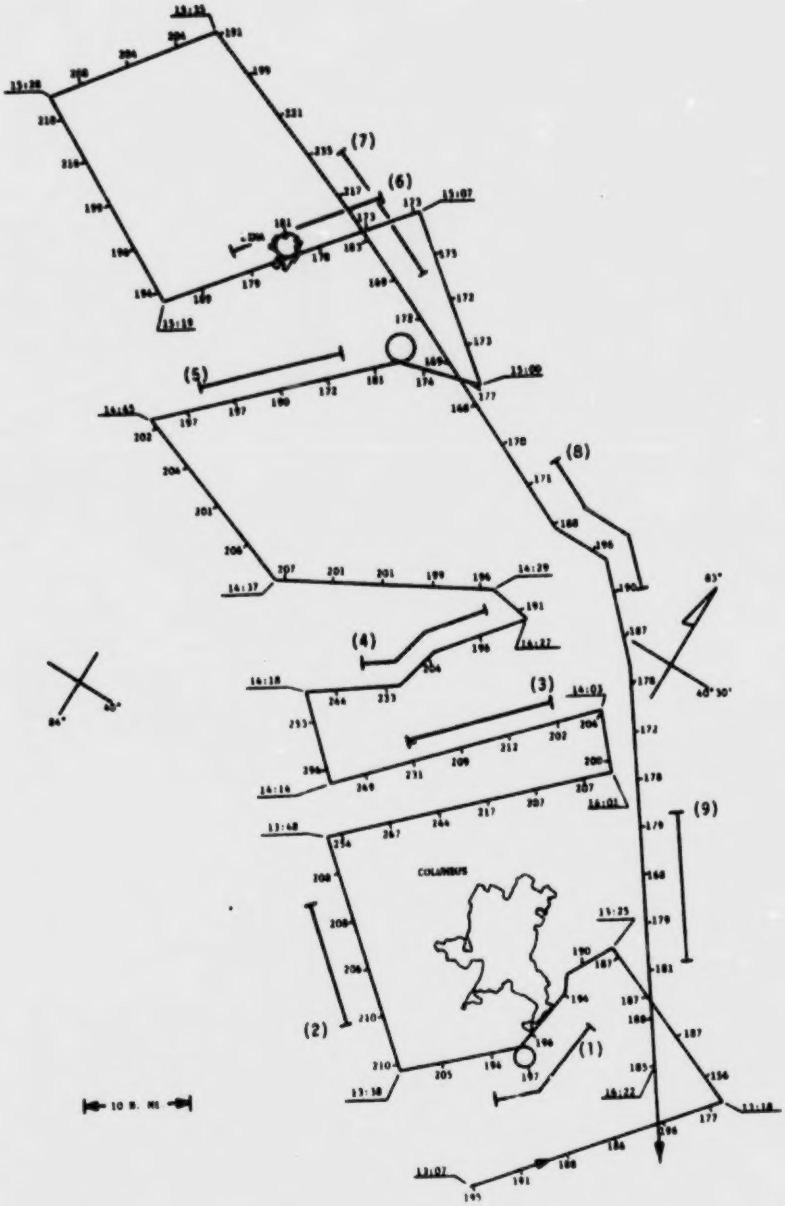
Variation of Ozone Concentrations Upwind, Over, and Downwind of the City

A comparison of average ozone concentrations on cross legs 3 through 6 shows an increase in ozone concentrations downwind of Columbus with a gradual decrease until at about 74 km (40 nm) downwind, concentrations were similar to those on the upwind legs.

Based primarily on nine, high data points to the northwest of Columbus, a sharply defined downwind plume containing high concentrations of ozone ($\sim$296 $\mu g/m^3$) is indicated. The plume axis lies (approximately) along the 278 degrees radial from Columbus, suggesting a transport wind from 98 degrees east of north. The plume seemed to be about 37 km (20 nm) wide with higher concentrations on the southeast edge (ozone concentrations at least 25 percent higher than elsewhere along the flight path). Surface wind peaks were small and from a northeast to east-southeast direction. Because of the irregular flight plan and misorientation with the apparent transport wind, further evidence of a city plume did not appear in the ozone data.

Variation of Hydrocarbon Concentrations and Ratios

Acetylene and isopentane concentrations for samples collected upwind and downwind of Columbus are shown in figure 50. Acetylene did increase downwind of the city, peaking in sample 4, 52 km (28 nm) from the city's center. It then fell off slowly until at 122 km (66 nm) downwind its concentration was about the same as the upwind concentration. Isopentane behaved in almost the reverse manner, being lower at the point at which acetylene peaked and much higher 122 km (66 nm) downwind in sample 6. Sample 6 was collected in the vicinity of Lima, and this city's influence, especially a


(1)
(2)
(3)
(4)
(5)
(6)
(7)
(8)
(9)
COLUMBUS
83°
40°30'
84°
40°
10 N. MI
13:07
13:18
13:25
13:38
13:48
14:03
14:14
14:18
14:22
14:29
14:37
14:45
15:00
15:07
15:19
15:28
15:35

FLIGHT DATE: July 25, 1974

TRUE AIRSPEED: 259.3 km/h (140 knots)

PATTERN: Square Wave

MISSION ALTITUDE: 762.0 meters (2,500 ft) above msl

LOW LEVEL WINDS:	
Sfc	070°/2.57 m/s (5 knots)
609 m (2,000')	135°/3.60 m/s (7 knots)
914 m (3,000')	130°/4.12 m/s (8 knots)
1219 m (4,000')	110°/4.12 m/s (8 knots)

DATA: Ozone Concentration in $\mu g/m^3$
Time in EDT
Hydrocarbon Sample Positions Denoted by |————| .

Low Level Winds From
National Weather Service
Upper Air Station
Dayton, Ohio-0800 EDT

Figure 49. Square wave flight of July 25, 1974.

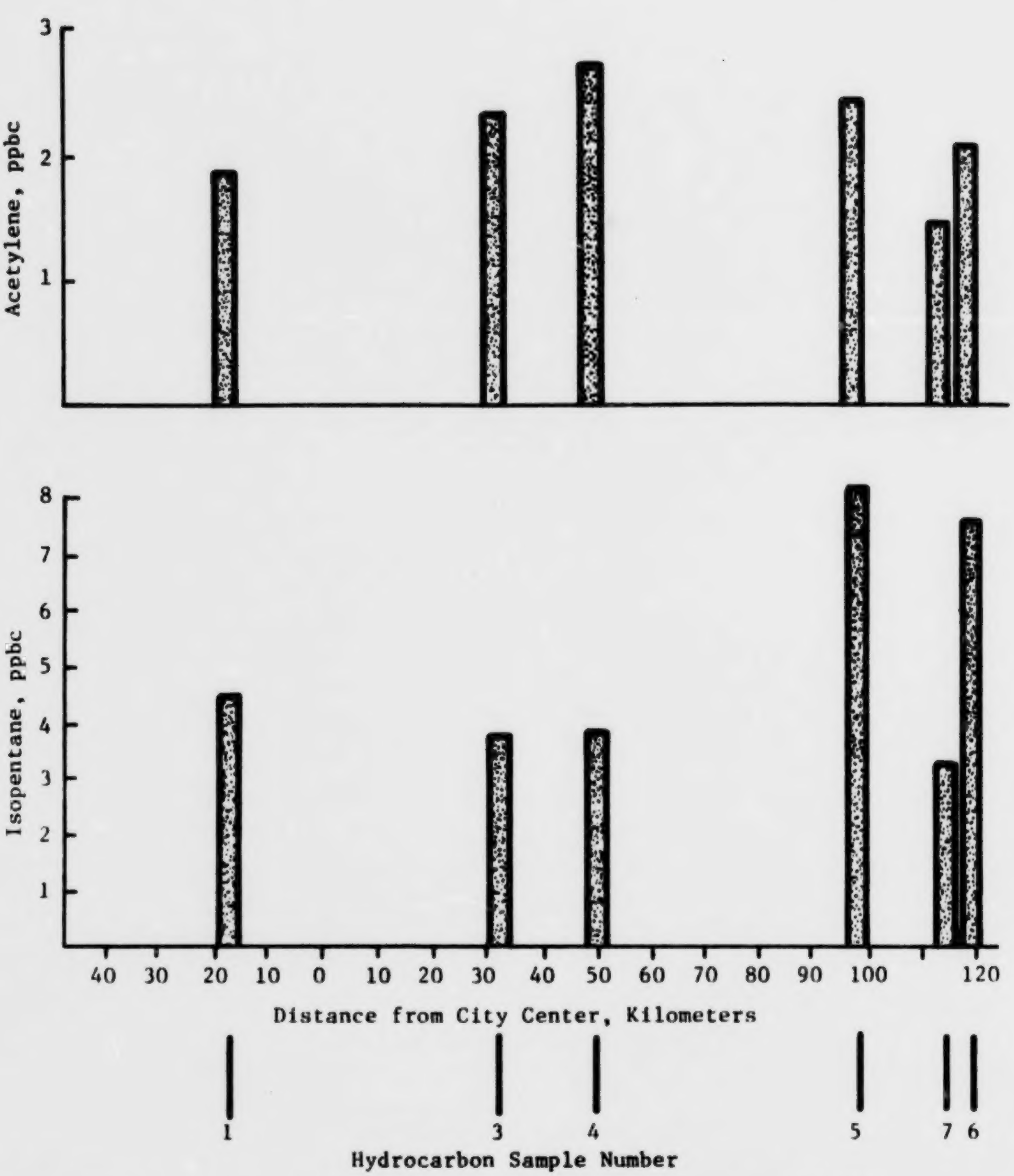


Figure 50. Acetylene and isopentane concentrations upwind and downwind of Columbus. Flight of July 25, 1974.

Table 19. Abstract of hydrocarbon data: Square wave flight of July 25, 1974.

Category	Sample number (time of sample collection-EDT)				
	1 (1329)	2 (1340)	3 (1405)	4 (1420)	5 (1449)
Ozone, $\mu g/m^3$	197	206	217	211	186
Acetylene, ppbc	1.8	2.6	2.3	2.7	2.4
Acetaldehyde/acetylene	2.0	1.7	1.5	1.8	1.5
Carbon monoxide, ppm	0.22	0.28	0.27	0.26	0.25
Carbon monoxide/acetylene	112.	108.	117.	96.	104.
Isobutylene/isobutane	0.3	0.1	0.3	0.3	---
Propylene/propane	0.1	0.2	0.5	0.3	0.4
Ethylbenzene/acetylene	<0.1	0.1	0.1	---	0.1
Propylene/acetylene	0.3	0.4	0.7	0.4	0.6

	6 (1509)	7 (1542)	8 (1557)	9 (1610)
Ozone, $\mu g/m^3$	177	190	191	175
Acetylene, ppbc	2.0	1.4	1.7	1.2
Acetaldehyde/acetylene	1.6	2.2	2.8	1.7
Carbon monoxide, ppm	0.25	0.26	0.23	0.22
Carbon monoxide/acetylene	125.	186.	164.	183.
Isobutylene/isobutane	0.3	0.5	0.5	0.7
Propylene/propane	0.6	0.3	0.3	0.2
Ethylbenzene/acetylene	0.1	---	---	---
Propylene/acetylene	2.8	1.1	0.8	0.9

tank storage area, could have been present here. The very large concentration of isopentane in sample 5 tends to substantiate this observation.

Comparison of Aircraft Data with Ground Station Data

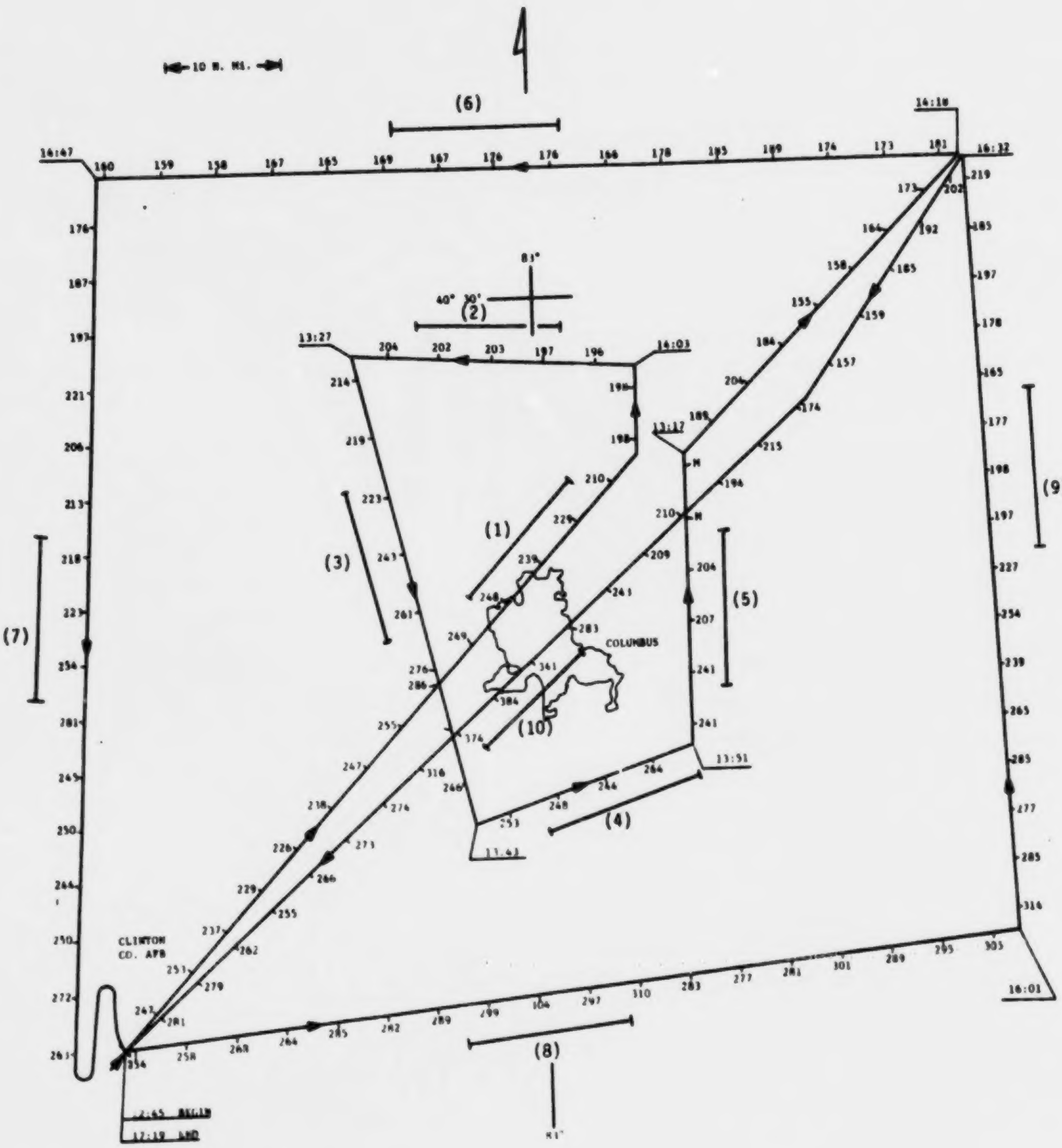
This flight passed over none of the rural ground stations. The wind at 750 m (2500 ft msl) was generally from the direction of the McConnelsville station. Examination of the diurnal curves for Columbus and McConnelsville show that the rural station attained higher ozone concentrations than the city station (170 vs 147 $\mu g/m^3$ at peak hourly average). The ozone concentrations measured by the aircraft instrument were higher on the average than either the city or the rural station. The low pass check of the airbrone ozone instrument showed it was reading from 15 to 19 percent higher than the Wilmington ground station instrument. The close check kept on calibration of instruments leads us to believe that this was a real difference.

6.1.2 Double Box Flights

The rationale for the use of the double box flight pattern has been presented in section 2 of this report. Three double box flights were examined for variations of ozone concentration in the areas of the city, the inner box, and the outer box. Also, the hydrocarbon samples were compared with one another and related to the average ozone concentration in the area where they were collected. When appropriate, meteorological conditions for the area are presented and pollutant behavior at the ground stations is discussed.

1. Double Box Flight of Saturday, July 6, 1974

The flight track is shown in figure 51. Hydrocarbon concentrations and ratios are given in table 20. Unfortunately, the hydrocarbon samples and their analyses are incomplete. The aircraft passed into and out of an area of haze several times; thus the meteorological summary in appendix C, figure C-5, should be examined. The distribution of temperature at flight level did not indicate a frontal zone aloft as the strong turning of the wind between 610 m (2000 ft) and 915 m (3000 ft) suggested. The air trajectories at 915 m (3000 ft) (see appendix F) for this time period showed a northwesterly flow into the area with a change toward easterly


4
10 n. mi.
(1)
(2)
(3)
(4)
(5)
(6)
(7)
(8)
(9)
(10)
14:47
14:18
16:32
13:27
14:03
13:17
13:51
13:41
16:01
81°
40° 30'
COLUMBUS
CLINTON CO. AFB
12:45 BEGIN
17:19 END

FLIGHT DATE: July 6, 1974

TRUE AIRSPEED: 277.8 km/h (150 knots)

PATTERN: Double Box

MISSION ALTITUDE: 762.0 m (2,500 ft) above msl

LOW LEVEL WINDS: Sfc 080°/2.57 m/s (5 knots)
609 m (2,000') 130°/3.60 m/s (7 knots)
914 m (3,000') 215°/2.06 m/s (4 knots)
1219 m (4,000') 290°/2.06 m/s (4 knots)

DATA: Ozone Concentration in μg/m^3
Time in EDT
Hydrocarbon Sample Positions Denoted by ├──────┤.

Low Level Winds From
National Weather Service
Upper Air Station
Dayton, Ohio-0800 EDT

Figure 51. Double box flight of July 6, 1974.

Table 20. Abstract of hydrocarbon data: Double box flight of July 6, 1974.

	Sample number (Time of sample collection-EDT)									
Category	1	2	3	4	5	6 (1430)	7	8	9 (1615)	10
Ozone, $\mu g/m^3$	*	*	*	*	*	173	*	*	185	*
Acetylene, ppbc						3.9			1.4	
Acetaldehyde/acetylene						1.4			5.5	
Carbon monoxide, ppm						---			---	
Carbon monoxide/acetylene						---			---	
Isobutylene/isobutane						0.4			0.4	
Propylene/propane						0.5			0.1	
Ethylbenzene/acetylene						0.1			0.6	
Propylene/acetylene						0.4			0.7	

*No data--analytical problem.

as the surface high-pressure system moved eastward. Surface winds at Dayton, Columbus, and Akron were northeast to easterly throughout most of the day. The 1300 EDT weather observation at Dayton showed that the visibility decreased from 13 km (8 miles) at 1000 to 8 km (5 miles) at 1300, and to 5 km (3 miles) by 1600. At the Columbus airport the visibility was never less than 13 km (8 miles) after 1000. At Akron and Cleveland, the visibility was essentially unlimited. The three hourly weather reports from Cincinnati Airport showed that visibility never exceeded 5 km (3 miles) after sunrise.

From the available data, no meteorological cause of the strong visibility gradient can be determined.

Diurnal Variation of Ozone Concentration

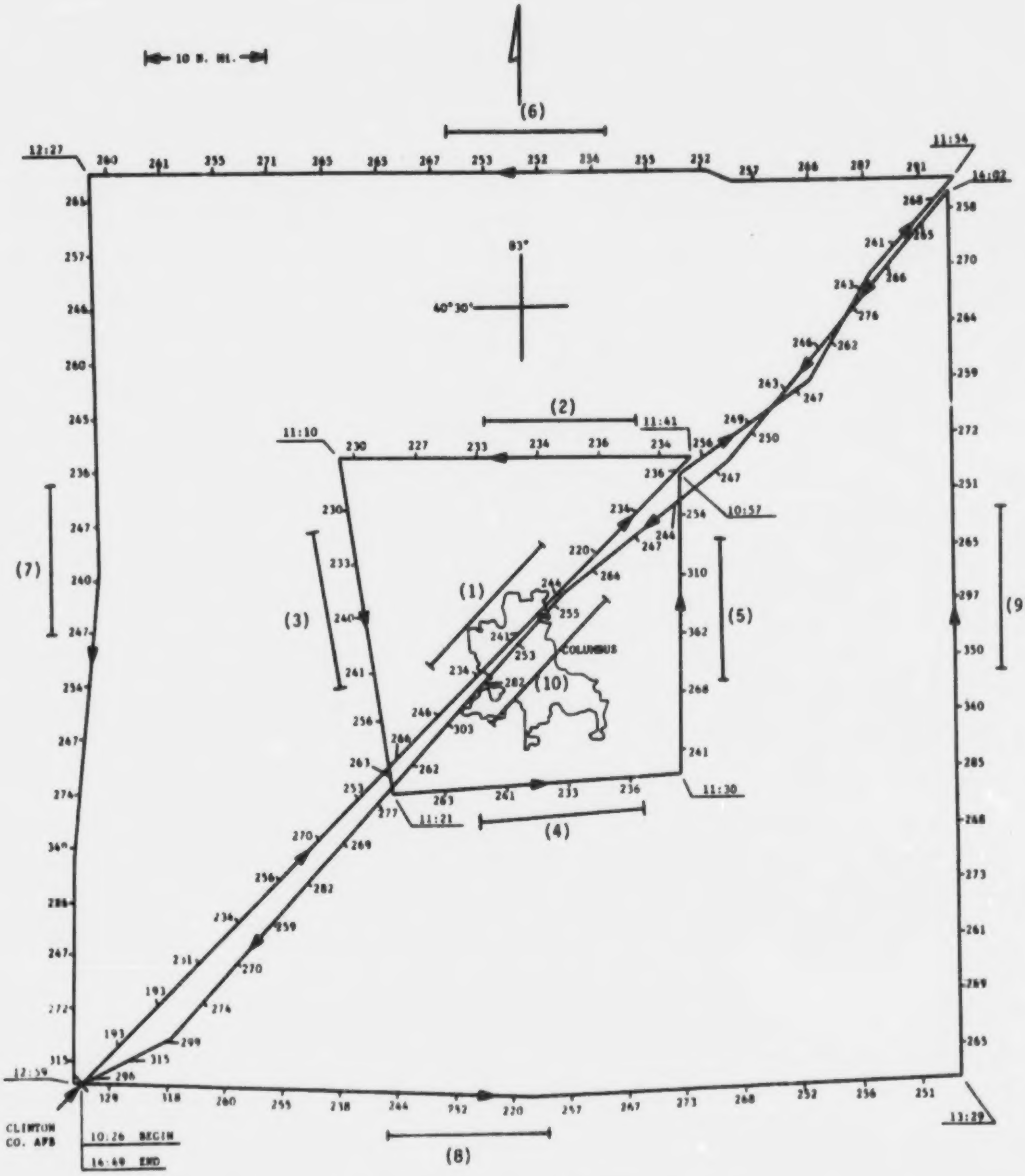
At most of the common locations in the flight plan the ozone concentrations were nearly identical. The principal exception is the return diagonal leg from Columbus to Wilmington, where concentrations increased over previous values by from 30 to 100 $\mu g/m^3$. These variations were most evident in the vicinity of the city.

Variation of Ozone Concentrations in Space

To the north of an east-west line approximately through Columbus, the average ozone concentrations were substantially less (200 $\mu g/m^3$ on leg 2 and 173 $\mu g/m^3$ on leg 6) than the 252 $\mu g/m^3$ on leg 5 and 286 $\mu g/m^3$ on leg 8. On legs 1, 7, 9, 3, 5, and 10, a sharp (≥ 30 $\mu g/m^3$) decrease of ozone occurred in the span of 4 minutes (18 km, 10 nm), as the aircraft moved from hazy to clear air. The change of visibility correlated with an increase of ozone concentration, suggesting that the haze (as well as the ozone) was of photochemical origin.

2. Double Box Flight of Tuesday, July 9, 1974

The flight pattern and measured ozone concentrations for the flight of July 9, 1974, are shown in figure 52. Hydrocarbon data are presented in table 21. On this day a broad area of high pressure covered the south-central and southeastern sections of the United State. A weak cold front lying on an east-west line through the Lake Superior region separated this high-pressure system from another high situated over the Hudson's Bay area of Canada.


10 N. MI.
(6)
12:27
260
261
255
271
265
265
267
253
252
256
255
252
257
266
287
291
11:54
14:02
265
257
266
260
265
236
247
240
247
254
267
274
34ᴺ
286
247
272
315
12:59
(7)
83°
40°30'
268
261
265
243
266
276
246
262
243
247
249
250
258
270
264
259
272
251
265
297
350
340
285
268
273
261
269
265
(9)
(2)
11:10
230
227
233
234
236
234
11:41
256
236
247
10:57
234
254
244
247
220
264
310
362
268
241
(5)
230
233
240
241
256
(3)
(1)
244
255
241
253
COLUMBUS
234
282
(10)
246
303
266
263
262
253
277
11:21
263
261
233
236
11:30
(4)
270
269
256
282
236
259
251
270
193
274
193
299
315
296
329
318
260
255
238
244
252
220
257
267
273
268
252
256
251
13:29
CLINTON CO. AFB
10:26 BEGIN
16:49 END
(8)

FLIGHT DATE: July 9, 1974

TRUE AIRSPEED: 277.8 km/h (150 knots)

PATTERN: Double Box

MISSION ALTITUDE: 762.0 m (2,500 ft) above msl

LOW LEVEL WINDS: Sfc	215°/2.06 m/s (4 knots)
609 m (2,000')	250°/4.63 m/s (9 knots)
914 m (3,000')	270°/3.09 m/s (6 knots)
1219 m (4,000')	285°/2.57 m/s (5 knots)

DATA: Ozone Concentration $\mu g/m^3$
Time in EDT

Hydrocarbon Sample Positions
Denoted by |———|

Low Level Winds From
National Weather Service
Upper Air Station
Dayton, Ohio-0800 EDT

Figure 52. Double box flight of July 9, 1974.

Table 21. Abstract of hydrocarbon data: Double box flight of July 9, 1974.

Category	Sample number (Time of sample collection-EDT)				
	1 (1046)	2 (1059)	3 (1113)	4 (1124)	5 (1133)
Ozone, $\mu g/m^3$	240	235	238	237	336
Acetylene, ppbc	3.8	2.3	2.1	1.9	8.9
Acetaldehyde/acetylene	3.1	2.4	3.5	9.3	0.9
Carbon monoxide, ppm	0.30	0.27	0.27	0.28	0.67
Carbon monoxide/acetylene	79.	117.	129.	147.	75.
Isobutylene/isobutane	0.6	0.2	0.5	0.4	0.5
Propylene/propane	0.3	0.2	0.1	0.2	0.3
Ethylbenzene/acetylene	0.3	0.4	0.1	0.1	0.2
Propylene/acetylene	0.5	0.4	0.2	0.6	0.4
	6 (1206)	7 (1239)	8 (1310)	9 (1344)	10 (1423)
Ozone, $\mu g/m^3$	253	245	239	323	263
Acetylene, ppbc	1.8	1.7	1.9	3.5	3.5
Acetaldehyde/acetylene	17.6	2.9	3.3	1.7	2.2
Carbon monoxide, ppm	0.25	0.26	0.22	0.38	0.32
Carbon monoxide/acetylene	139.	153.	116.	109.	91.
Isobutylene/isobutane	0.4	0.4	0.5	0.6	0.3
Propylene/propane	0.1	0.2	0.1	0.1	0.1
Ethylbenzene/acetylene	0.3	0.2	0.1	0.1	0.3
Propylene/acetylene	0.3	0.5	0.3	0.3	0.2

Wind conditions over the Columbus area are given in table 22. In general the wind direction veered with height and remained within the 2.5 to 5 m/sec (5 to 10 mph) speed range. It is of interest to note that the surface wind at Columbus backed from 250° at the beginning of the flight to approximately 130° at the end of the flight period. The increase in wind speed to 7.5 m/sec (15 mph) during mid-afternoon can be considered to remove this flight from the "stagnating high pressure system" category. However, this speed increase may have been transitory and local as is suggested by the measured speeds of 5 m/sec (10 mph) or less shown in both the 0800 and 2000 EDT upper wind observations at Dayton, Ohio. The backing of the wind with time in both the upper wind and surface observations was probably associated with the development of a trough of low pressure over the southern Appalachians during this period and the development of a ridge of high pressure east of Columbus.

Diurnal Variation of Ozone Concentration

The ozone concentration measurements from this flight were first examined for evidence of a time trend in the data to determine if a correction should be applied to negate the effect of the normal afternoon increase in ozone concentrations usually found in surface-level measurements. Figure 53 shows a comparison of the ozone concentrations measured on the flights along the diagonal of the double box pattern from southwest to northeast from 1026 EDT to 1154 EDT* and from northeast to southwest from 1402 EDT to 1449 EDT. No time trend of increasing ozone is evident in the data shown in figure 53, although there is a separation of at least two hours between the measurements making up the data pairs. The divergence of the data points at the southwestern end of the flight can probably be associated with altitude changes during ascent and descent from and to the base station at Wilmington. Based on this analysis, the measured ozone concentrations were used without correction for a trend with time.

---

*This flight was interrupted to fly the pattern of the inner box and, consequently, took longer to complete than did the uninterrupted return flight. See flight pattern, appendix C, flight C-6.

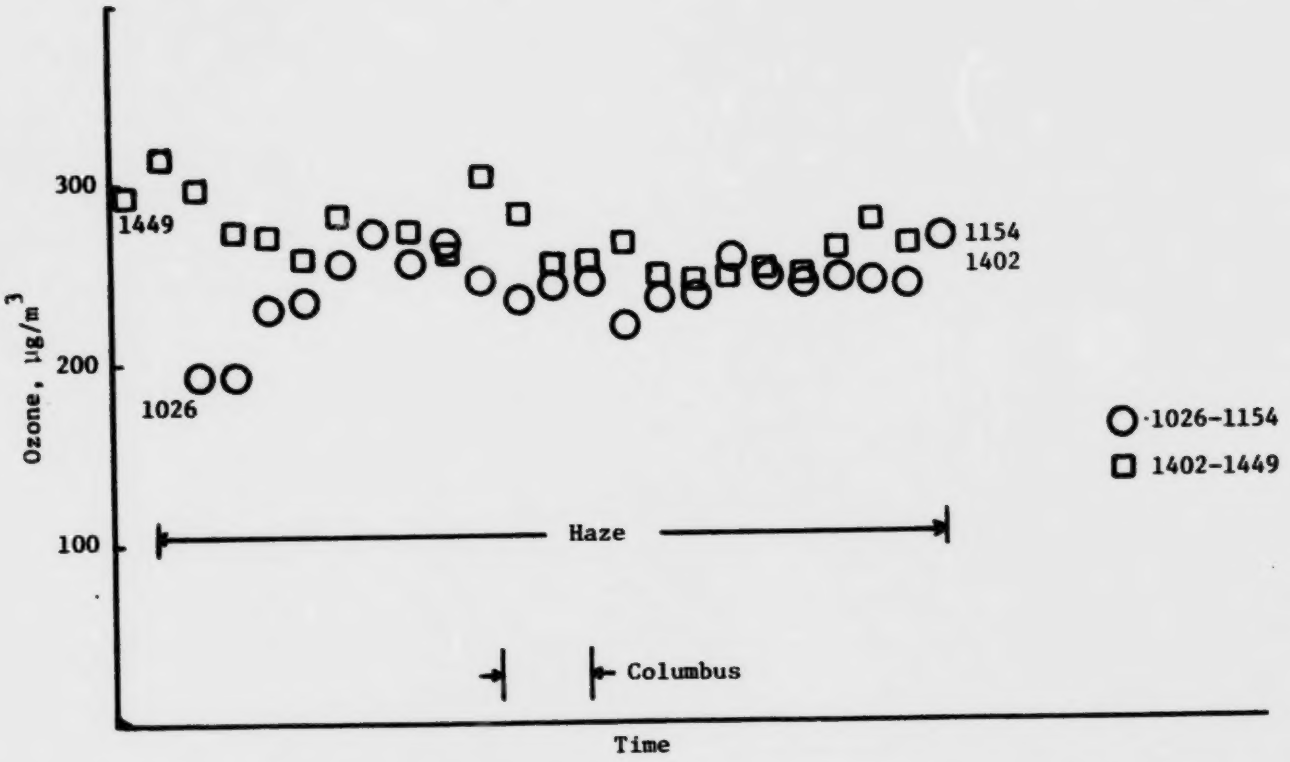


Figure 53. Ozone concentrations along diagonal flight legs. Flight of July 9, 1974.

Table 22. Wind observations, July 9, 1974

Altitude m (ft), MSL	Dayton						Columbus								
	0700 EDT			2000 EDT			1100 EDT			1400 EDT			1700 EDT		
	Deg.	m/sec	MPH	Deg.	m/sec	MPH	Deg.	m/sec	MPH	Deg.	m/sec	MPH	Deg.	m/sec	MPH
Surface	215	2.2	(5)	120	3.6	(8)	250	3.1	(7)	130	6.7	(15)	140	1.8	(4)
600 (2000)	250	4.4	(10)	230	4.0	(9)									
900 (3000)	270	3.1	(7)	240	3.6	(8)									
1200 (4000)	285	2.7	(6)	255	3.1	(7)									

Other Ozone Variations

The ozone concentrations on the eight legs of the flight (each side of each box pattern being considered a flight leg) were examined to determine if there were recognizable differences in the fields of ozone concentrations from which these sets of samples had been drawn. The results are summarized in table 23. For convenience, the legs of the flight have been numbered sequentially counterclockwise, starting with the northern side of the inner box as number 1 and the northern side of the outer box as number 5.

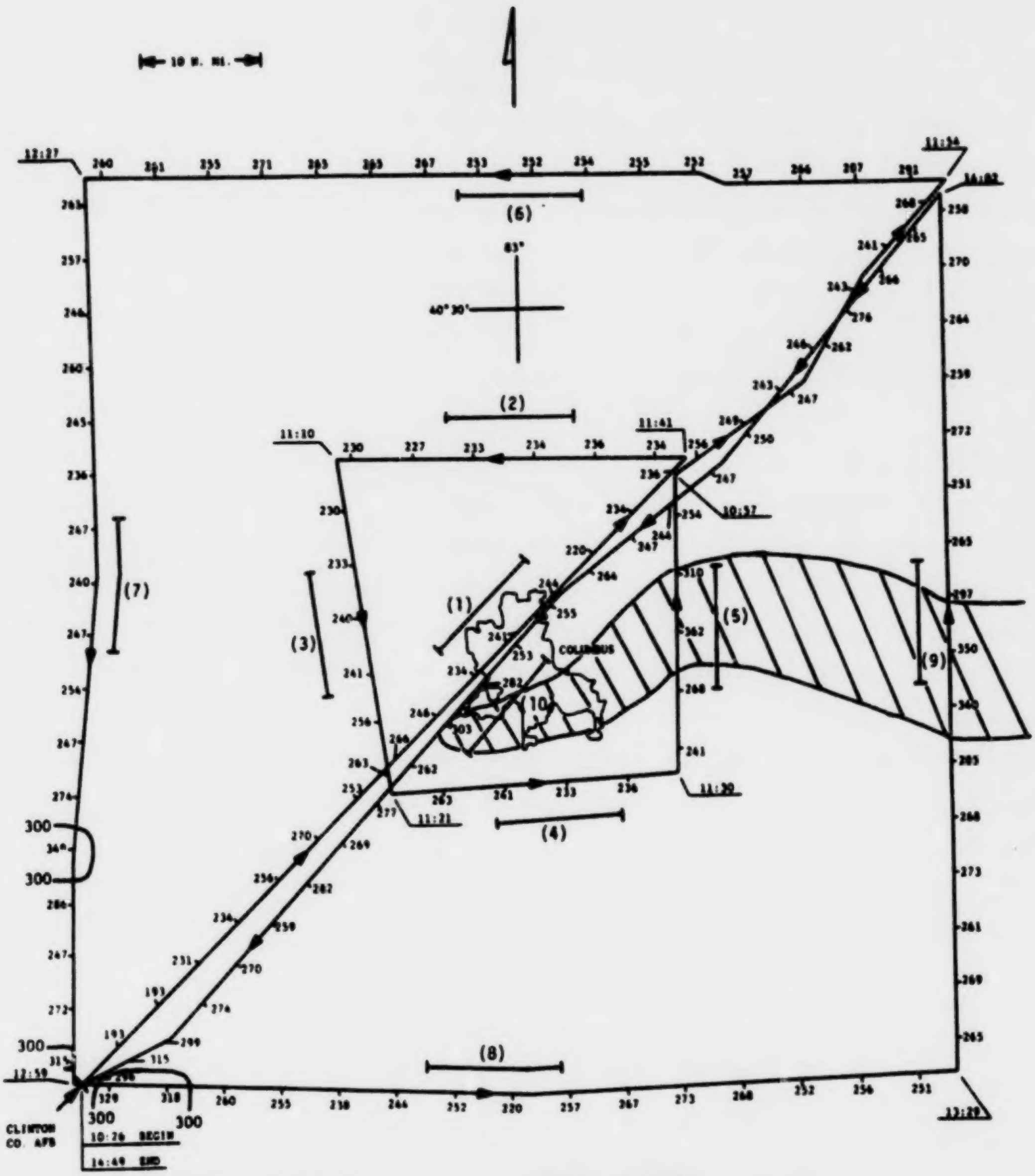
Several features stand out in the statistics given in table 23. Excluding leg 4 (inner box) and leg 8 (outer box), the average concentrations of ozone around the inner box are on the order of 10 percent less than around the outer box, and the average deviations from those average concentrations are about twice as large around the outer box. The extreme deviation from the average concentration in each case is positive, that is, a higher-than-average concentration.

The average concentrations along flight legs 4 and 8 differ from the average concentrations on the other three legs of their boxes by about 20 and 6 percent, respectively.

When the ozone concentration measurements are plotted in their appropriate geographic relationship (figure 54) it appears that there is a

Table 23. Characteristics of ozone concentration distributions by flight leg - July 9, 1974

Flight Leg	No. of Obs.	Average Concentration ($\mu g/m^3$)	Av. Dev. from Average	No. of Dev.		Max. Dev. ($\mu g/m^3$)	
				+	-	+	-
1	6	232	2.7	4	2	4	5
2	6	244	10.5	2	4	19	14
3	4	243	9.8	1	3	20	10
4	5	287	39.2	3	2	75	46
5	16	263	8.7	7	9	28	11
6	17	264	21.0	5	12	85	28
7	15	263	19.0	8	7	66	43
8	16	278	20.0	12	4	72	27


10 N. MI.
N
12:27
11:54
14:02
11:10
11:41
10:57
11:30
11:21
12:59
13:29
(1)
(2)
(3)
(4)
(5)
(6)
(7)
(8)
(9)
(10)
83°
40°30'
COLUMBUS
CLINTON CO. AFB
10:26 BEGIN
14:49 END
300
300
300
300

FLIGHT DATE: July 9, 1974

PATTERN: Double Box

TRUE AIRSPEED: 277.8 km/h (150 knots)

MISSION ALTITUDE: 762.0 m (2,500 ft) above msl

LOW LEVEL WINDS:	
Sfc	215°/2.06 m/s (4 knots)
609 m (2,000')	250°/4.63 m/s (9 knots)
914 m (3,000')	270°/3.09 m/s (6 knots)
1219 m (4,000')	285°/2.57 m/s (5 knots)

DATA: Ozone Concentration µg/m^3
Time in EDT
Hydrocarbon Sample Positions
Denoted by

Low Level Winds From
National Weather Service
Upper Air Station
Dayton, Ohio-0800 EDT

Figure 54. Suggested plume from Columbus: flight of July 9, 1974.

correlation between the high values of ozone concentrations observed on legs 4 and 8. An area of ozone concentration greater than 300 $\mu g/m^3$ can be depicted as shown by the hatched area in the figure. Considering the west to southwesterly winds at flight level, this area of high ozone concentration can be construed as an ozone plume emanating from Columbus. The hydrocarbon data, as exemplified by the acetylene concentrations, correlate well with these observations. The two inner-city acetylene concentrations were 3.8 and 3.5 ppbc. To the east the concentration or the inner leg of the pattern was 8.9 ppbc; the concentration on the outer box was 3.5 ppbc. Concentrations on the north, west, and south legs of both inner and outer boxes ranged from 1.7 to 2.3 ppbc. There is also an ozone concentration value of 349 $\mu g/m^3$ along the last quarter of leg 6 and several measurements of concentrations slightly in excess of 300 $\mu g/m^3$ in the vicinity of the turn from leg 6 to leg 7. These high concentrations of ozone cannot be attributed to Columbus. However, Dayton is approximately 32 km almost due west of the measurement of 349 $\mu g/m^3$ ozone, and Cincinnati is southwest of Columbus, practically along an extension of the diagonal flight path through the boxes, and approximately 59 km from the > 300 $\mu g/m^3$ measurements. If this association of ozone concentrations with urbanized areas has validity, a conditions such as shown schematically in figure 55 might arise at flight level (762 m, 2500 ft, MSL) with a windspeed of 3.6 m/sec (8 mph).

3. Double Box Flight of July 13, 1974

On July 13, 1974, the double box flight pattern originated at 1100 at Wilmington, Ohio. The flight ended at 1518 EDT. The flight altitude 762 m (2500 feet) MSL; the true air speed was 69 m/sec (135 knots). Winds, as measured by the Dayton RAOB station were:

SFC	130° 2 m/sec (4 kt)
600 m (2000 ft)	205° 3 m/sec (6 kt)
900 m (3000 ft)	145° 1 m/sec (2 kt)
1200 m (4000 ft)	075° 1 m/sec (2 kt)

Ten hydrocarbon bag samples were collected during the flight. Ozone was measured continually. The flight track is shown in figure 56. Hydrocarbon concentrations and ratios are summarized in table 24.

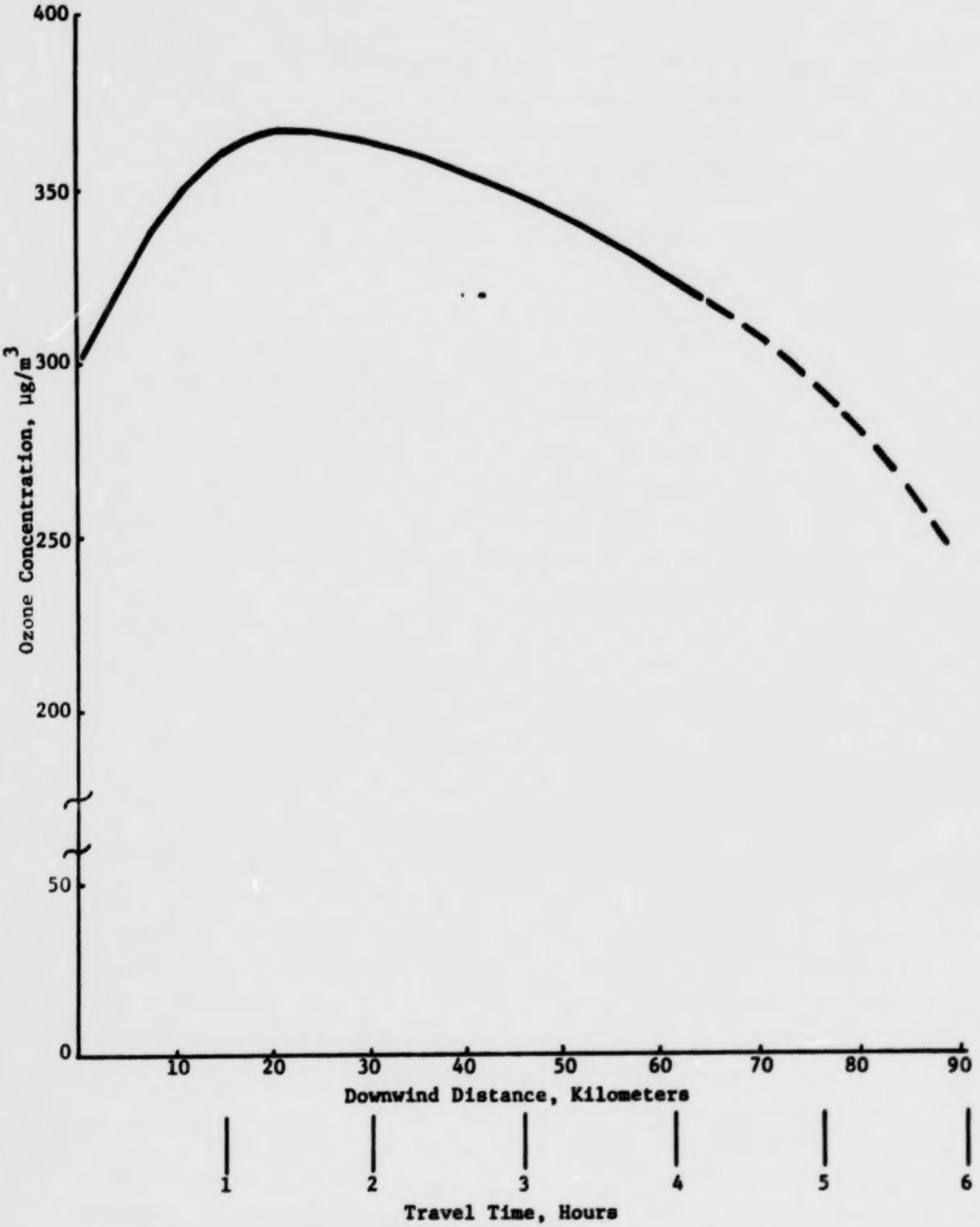
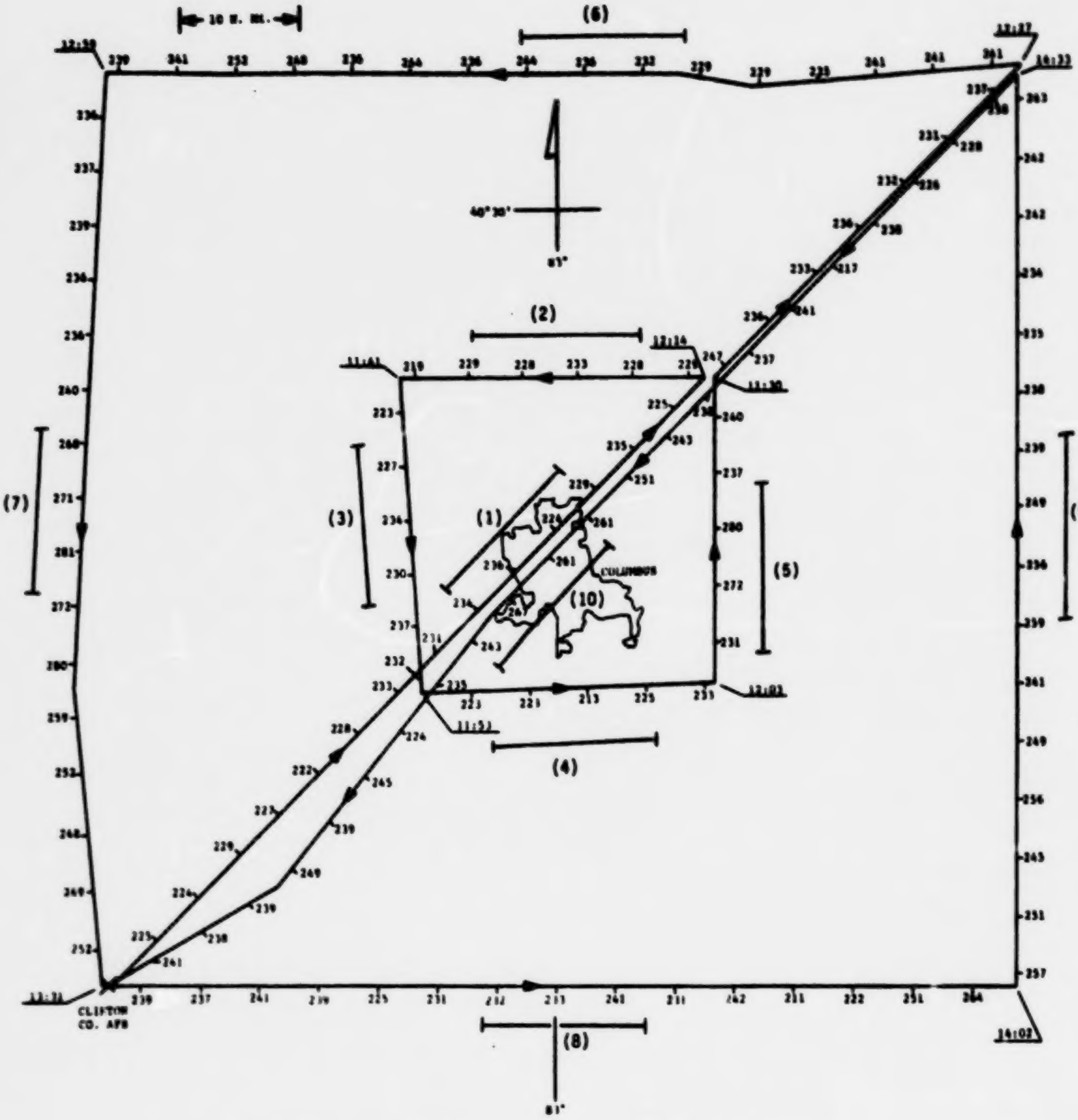


Figure 55. Ozone concentrations at 762 m (2500 ft) msl downwind of an urban area. Curve has been synthesized from the highest ozone concentrations attributed to Columbus, Dayton and Cincinnati in the discussion of the flight of July 9, 1974. Windspeed, 3.6 m/sec (8 mph).


10 N. MI.
(6)
12:30
12:37
14:33
40°30'
81°
(2)
12:14
11:41
11:30
(7)
(3)
(1)
COLUMBUS
(10)
(5)
(9)
12:03
11:53
(4)
CLIFTON
CO. AFB
(8)
14:02
81°

FLIGHT DATE: July 13, 1974

PATTERN: Double Box

TRUE AIRSPEED: 250.0 km/h (135 knots)

MISSION ALTITUDE: 762.0 m (2,500 ft) above msl

LOW LEVEL WINDS:	Sfc	130°/2.06 m/s (4 knots)
	609 m (2,000')	205°/3.09 m/s (6 knots)
	914 m (3,000')	145°/1.03 m/s (2 knots)
	1210 m (4,000')	075°/1.03 m/s (2 knots)

DATA: Ozone Concentration in μg/m^3
Time in EDT

Hydrocarbon Sample Positions
Denoted by ├────┤.

Low Level Winds From
National Weather Service
Upper Air Station
Dayton, Ohio-0800 EDT

Figure 56. Double box flight of July 13, 1974.

Table 24. Abstract of hydrocarbon data: Double box flight of July 13, 1974.

Category	Sample number (Time of sample collection-EDT)				
	1 (1118)	2 (1132)	3 (1144)	4 (1156)	5 (1205)
Ozone, $\mu g/m^3$	231	230	230	220	255
Acetylene, ppbc	2.8	2.3	1.7	2.5	6.4
Acetaldehyde/acetylene	2.4	2.7	3.2	2.5	1.3
Carbon monoxide/ppm	0.24	0.21	0.23	0.28	0.49
Carbon monoxide/acetylene	86.	91.	135.	112.	77.
Isobutylene/isobutane	0.4	0.5	0.4	0.4	0.3
Propylene/propane	0.1	0.2	0.2	0.1	0.1
Ethylbenzene/acetylene	-	-	~0.4	0.2	0.2
Propylene/acetylene	0.4	0.4	0.6	0.4	0.3
	6 (1239)	7 (1311)	8 (1343)	9 (1414)	10 (1454)
Ozone, $\mu g/m^3$	237	273	235	251	263
Acetylene, ppbc	1.7	3.1	1.9	2.4	2.5
Acetaldehyde/acetylene	2.9	2.5	2.5	2.0	3.7
Carbon monoxide/ppm	0.23	0.34	0.24	0.24	0.30
Carbon monoxide/acetylene	135.	110.	126.	100.	120.
Isobutylene/isobutane	0.2	0.3	0.3	0.3	0.3
Propylene/propane	0.2	0.1	0.2	0.2	>0.5
Ethylbenzene/acetylene	~0.5	0.2	0.3	0.7	>0.1
Propylene/acetylene	0.7	0.3	0.5	0.8	1.3

Diurnal Variation of Ozone Concentration

There appears to be little diurnal variation along the flight path during this time frame. This statement is based on the small change in the average ozone concentration (231 $\mu g/m^3$) for the initial diagonal extending from Wilmington to the northeast as compared to the concentration (242 $\mu g/m^3$) on the same diagonal on the home-bound leg at the end of the flight, which ended 3 hours after completion of the first diagonal.

There does, however, seem to be a significant diurnal change in the ozone concentrations (along a portion of the same diagonals) taken over Columbus. The three values recorded earlier in the day (around 1118) averages 231 $\mu g/m^3$; later in the day (around 1454) the average was 263 $\mu g/m^3$. This would be expected behavior for a somewhat stagnant air mass above a city; in other words, it reflects the more dramatic diurnal behavior of an air mass above the city as compared to the 762 m (2500 ft) level variations throughout the general area of the double box pattern.

Variation of Ozone Concentrations; Inner Box Versus Outer Box

The overall average of the ozone concentration along the four sides of the inner box is 234 $\mu g/m^3$. The corresponding average for the outer box is 244 $\mu g/m^3$. This result suggests that the inner box is more under the city's influence than is the outer box. However, the difference between the ozone average of inner and outer box is only 10 $\mu g/m^3$.

Other Variations in Ozone Concentrations

There were two ozone "hot spots" in two of the box sides. One was on the eastern leg of the inner box where, over at least a 9 km (5 nm) path, the ozone concentration was greater than 272 $\mu g/m^3$. The second was on the western leg of the outer box where the ozone concentration averaged 274 $\mu g/m^3$ over a 37 km path. Both these high ozone spots occurred during the part of the flight track where hydrocarbon samples were being collected. The hydrocarbon content of the bags is discussed below. The inner-box ozone "hot spot" probably can be attributed to Columbus while that in the outer box probably reflects precursor injection from upwind (i.e., from somewhere other than Columbus.

Comparison of Various Hydrocarbon Concentrations and Ratios with Ozone Concentrations

Hydrocarbon samples 1 and 10 were taken over the city of Columbus, approximately 3.5 hours apart. During this span of time, the average ozone concentration over the city increased from 231 to 263 $\mu g/m^3$.

The acetylene concentrations were about the same in the two samples, 2.8 and 2.5 ppbc. However, there was some doubt of the validity of the acetylene concentration in the analysis. The carbon monoxide concentration was 344 $\mu g/m^3$ in sample 1 and 366 $\mu g/m^3$ in sample 10. Each of the hydrocarbons n-butane, isopentane, and n-pentane (which were analyzed on a different chromatographic column and whose concentrations are considered valid) show an increase with time when samples 1 and 10 are compared. A similar increase is noted for each of the oxygenated compounds, acetaldehyde, propionaldehyde, and acetone. An increase also occurred in the unsaturated compounds, isobutylene.

All these increases could be expected to occur in the air over a city while stagnant-air conditions were prevalent. The hydrocarbon concentrations would build due to emissions and to evaporative processes; the oxygenated compounds would increase due to oxidation of hydrocarbons both by combustion and in atmospheric photochemical processes.

Average concentrations for gases in the four samples of the inner box were 7.7 ppbc for isopentane, 3.2 ppbc for acetylene, 9.2 ppbc for n-butane, 3.4 ppbc for n-pentane, and 1.4 ppbc for isobutylene. The highest concentration in each case occurred in sample 5, which incidentally was obtained in the area of high ozone discussed earlier. The corresponding averages for the four samples of the outer box were 4.8 ppbc for isopentane, 2.3 ppbc for acetylene, 6.1 ppbc for n-butane, 2.5 ppbc for n-pentane, and 0.75 ppbc for isobutylene. In each case, the average concentration was lower than that of the inner box. Also, the highest concentration in each case occurred in sample 7, again a sample taken in a high ozone area.

The average concentrations for gases in the four samples of the inner box for the oxygenated compounds acetaldehyde, propionaldehyde, and acetone were 6.6, 2.6, and 6.9 ppbc, respectively. The highest concentration for each occurred in sample 5. The average concentrations for the same oxygenated compounds in the outer box were 5.6, 2.6, and 12.2 ppbc. The highest concentration for each occurred in sample 7. The concentrations of oxygenated compounds were about the same in the inner and outer boxes for acetaldehyde and propionaldehyde; acetone was much higher in the outer box.

The similarity in concentrations for the oxygenated compounds suggests that their presence away from the city is dependent on injection of hydrocarbons from the city followed by photooxidation. The direct emissions of these compounds from sources in the countryside surrounding the city cannot at this time be ruled out, nor can the possibility that there was an appreciable "residue" of compounds from a prior day's emission from Columbus.

6.1.3 Eastern Flight of August 21, 1974

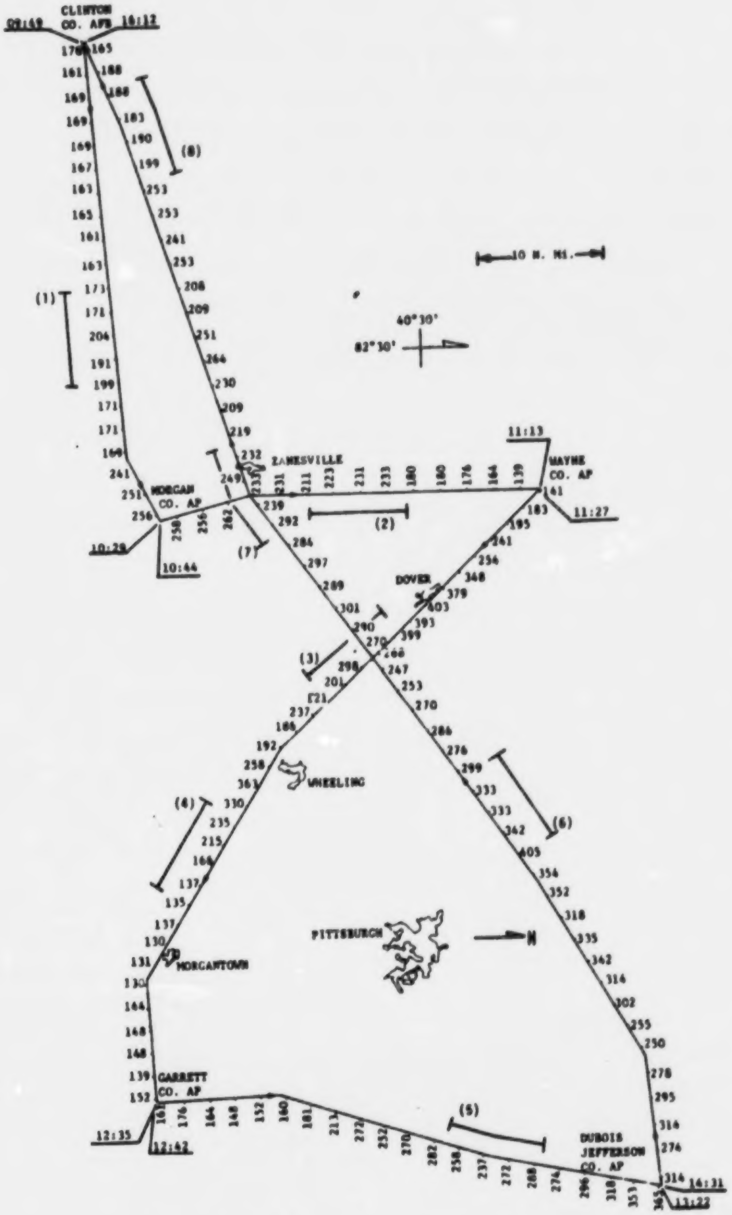
The purpose of this flight was to examine variations in ozone concentration over a widespread area under stagnant-air conditions. The aircraft departed from Wilmington at 0949. The flight was flown at 1200 m (4000 ft) msl at a true air speed of 69 m/sec (135 knots). The 1200 m (4000 ft) winds at 0700 measured at the Dayton RAOB Station were from the southeast at 2.6-5.1 m/sec (5-10 knots). The total time of the mission was 6 hours. Eight hydrocarbon bag samples were collected in the areas indicated on the flight track shown in figure 57. Hydrocarbon concentrations and ratios are summarized in table 25. The flight path was planned so that a large area could be surveyed for ozone while allowing the plane to pass over each of the ground stations.

Diurnal Variation of Ozone Concentration

It is difficult to establish whether diurnal variation occurred during this flight since only at two points did the flight pattern pass through the same airspace. At one of these crossover points, the later ozone concentration was 6 $\mu g/m^3$ higher than the earlier concentration (239 versus 233). At the other crossover point, the later ozone concentration was 21 $\mu g/m^3$ lower than the earlier value (247 versus 268). If the average concentration for the flight from Wilmington to McConnelsville (Wayne County Airport) is compared with the corresponding portion of the return flight (about 32 km further north), an increase of 36 $\mu g/m^3$ ozone is seen. These flight portions were flown about 5 hours apart. Whether this finding could support the idea of significant diurnal variation is questionable.

High Ozone Concentrations During the Flight

An area existed near McConnelsvilee (Morgan County Airport) where five consecutive ozone measurements averaged 262 $\mu g/m^3$. The average for the


CLINTON CO. AFB
09:49
16:12
10 N. Mi.
40°30'
82°30'
ZANESVILLE
WAYNE CO. AP
11:13
11:27
MORGAN CO. AP
10:29
10:44
DOVER
WHEELING
PITTSBURGH
N
MORGANTOWN
GARRETT CO. AP
12:35
12:42
DUBOIS JEFFERSON CO. AP
14:31
13:22
(1)
(2)
(3)
(4)
(5)
(6)
(7)
(8)

FLIGHT DATE: August 21, 1974

PATTERN: Eastern Stagnation Ground Station Interlock

TRUE AIRSPEED: 250 km/h (135 knots)

MISSION ALTITUDE: 1219 m (4000 ft) above msl

LOW LEVEL WINDS:	Sfc	140°/2.06 m/s (4 knots)
	609 m (2000')	145°/5.66 m/s (11 knots)
	916 m (3000')	130°/6.69 m/s (13 knots)
	1219 m (4000')	140°/6.69 m/s (13 knots)

DATA: Ozone Concentration in $\mu g/m^3$
Time in EDT

Hydrocarbon Sample Positions
Denoted by ├──────┤ .

Low Level Winds From
National Weather Service
Upper Air Station
Dayton, Ohio-0800 EDT

Figure 57. Eastern flight of August 21, 1974.

Table 25. Abstract of hydrocarbon data: eastern flight of August 21, 1974

Category	Sample number (time of sample collection-EDT)							
	1 (1010)	2 (1056)	3 (1147)	4 (1207)	5 (1304)	6 (1500)	7 (1530)	8 (1600)
Ozone, $\mu g/m^3$	204.	233.	298.	215.	258.	342.	292.	193.
Acetylene, ppbc	1.7	1.9	2.8	1.8	2.8	6.9	2.8	1.3
Acetaldehyde/acetylene	2.	1.	1.	2.7	1.	0.9	1.	2.
Carbon monoxide, ppm	-	-	-	-	-	-	-	-
Carbon monoxide/acetylene	-	-	-	-	-	-	-	-
Isobutylene/isobutane	0.4	0.2	0.5	0.4	0.5	0.2	0.3	0.6
Propylene/propane	0.5	0.2	0.7	0.8	0.7	0.3	0.2	1.0
Ethylbenzene/acetylene	0.1	0.2	0.3	0.1	0.3	0.4	0.3	0.3
Propylene/acetylene	0.6	0.4	1.1	1.2	1.1	0.3	0.4	2.

five consecutive preceeding measurements was only 180 $\mu g/m^3$. In the flight log it was noted that the area was particularly hazy, and several industrial plumes (power plants and others) could be clearly observed, and the odor of one (a pulp mill) was detected. It is possible that the ozone enhancement could have been caused by photochemistry involving effluents from these sources. The ground-station ozone concentration at the same time (1015-1030) however, was only 45 $\mu g/m^3$. Evidently, some stratification of ozone generative-ability existed.

A second "hot spot" occurred on the flight track leaving the Wayne County Airport over the city of Dover, Ohio. The average for four ozone measurements here was 393 $\mu g/m^3$. The four preceding points averaged only 259 $\mu g/m^3$.

A third high ozone area was located just south of the DuBois-Jefferson County Airport. The last two measurements before landing averages 359 $\mu g/m^3$. The preceding five measurements averaged only 290 $\mu g/m^3$. Concentration of ozone at the ground station was approaching 310 $\mu g/m^3$ at this time. In fact, DuBois had the highest diurnal peak for all stations, rural or urban, measured that day.

Another elevation in ozone concentration occurred as the plane passed northwest of Pittsburgh, about 50 km (30 nm) downwind of the city. It is significant that winds were from the southeast that day. A peak concentration of 405 $\mu g/m^3$ was observed. The influence of the Pittsburgh city "plume" is probable here. The hydrocarbon sample taken near this point also showed elevated values of acetylene, other hydrocarbons, and carbon monoxide, again pointing to the influence of the city.

Comparison of Aircraft Data with Ground Station Data

In general, ozone concentrations were high (i.e., > 180 $\mu g/m^3$) at all ground stations during the portion of the day between 1600-1800.

At Wilmington, the average hourly ozone concentration from 0900-1000 was 76 $\mu g/m^3$ when the airplane departed. The ozone concentrations at 1220 m (4000 ft) msl ranged from 160-170 $\mu g/m^3$ as the plane departed.

On the return flight, about 6 hours later, ozone concentration near Wilmington averaged 183 $\mu g/m^3$ in the 1500-1600 hour; ground concentration averaged about 205 $\mu g/m^3$. Ozone concentrations at Wilmington reached a high of 209 $\mu g/m^3$ that day in the 1500 hour.

Near the Wayne County Airport (Wooster) ozone concentrations averaged about 140 $\mu g/m^3$ in the 1100-1200 hour. The corresponding ground concentration during the same time frame was approximately 110 $\mu g/m^3$. The high for the day at Wooster was 233 $\mu g/m^3$, occurring in the 1800 hour.

Near Garrett County, Maryland, ozone concentrations averaged 157 $\mu g/m^3$ during the 1200-1300 hour; ground concentrations were about 155 $\mu g/m^3$. The high concentration for the day was about 189 $\mu g/m^3$ and occurred during the 1800 hour.

Near the DuBois-Jefferson County Airport, the ozone concentrations just before the aircraft landed averaged 379 $\mu g/m^3$. The ground concentration was about 310 $\mu g/m^3$. The high for the day was 329 $\mu g/m^3$, which was the highest concentration recorded at any of the ground stations, rural or urban, for that day.

Pittsburgh and Columbus had peak ozone concentrations of about 188 and 176 $\mu g/m^3$ for the hours ending at 1600 and 1900, respectively.

6.1.4 Vertical Flights

Vertical flights were made on June 25, July 17, August 1, and August 15 over Wilmington and, on August 13, over Wooster and McConnelsville. Flight tracks and ozone data for these vertical flights are presented in figures in appendix C. Ozone data for the vertical flights flown on August 1, 1974, are presented in figure 58. Hydrocarbon concentrations and ratios for vertical flights where grab samples were collected are summarized in tables 26, 27, and 28.

The vertical profiles were all flown in the morning, except for the "noon" and "evening" flights on August 1, 1974. On the latter two flights, no hydrocarbon bag samples were collected.

In the mornings, in all cases, the ozone concentration aloft was higher than the ground-station concentration and increased with altitude and usually appeared to peak somewhere between 610 m (2000 ft) and 1830 m (6000 ft). At still higher elevations, the concentrations decreased. This is interpreted as being due to destruction of ozone in the nocturnal radiation layer, preservation of ozone (with only slight destruction) in the remnant of the previous day's mixing layer above the radiation inversion, and lower concentrations still further aloft. The ozone at these highest altitudes

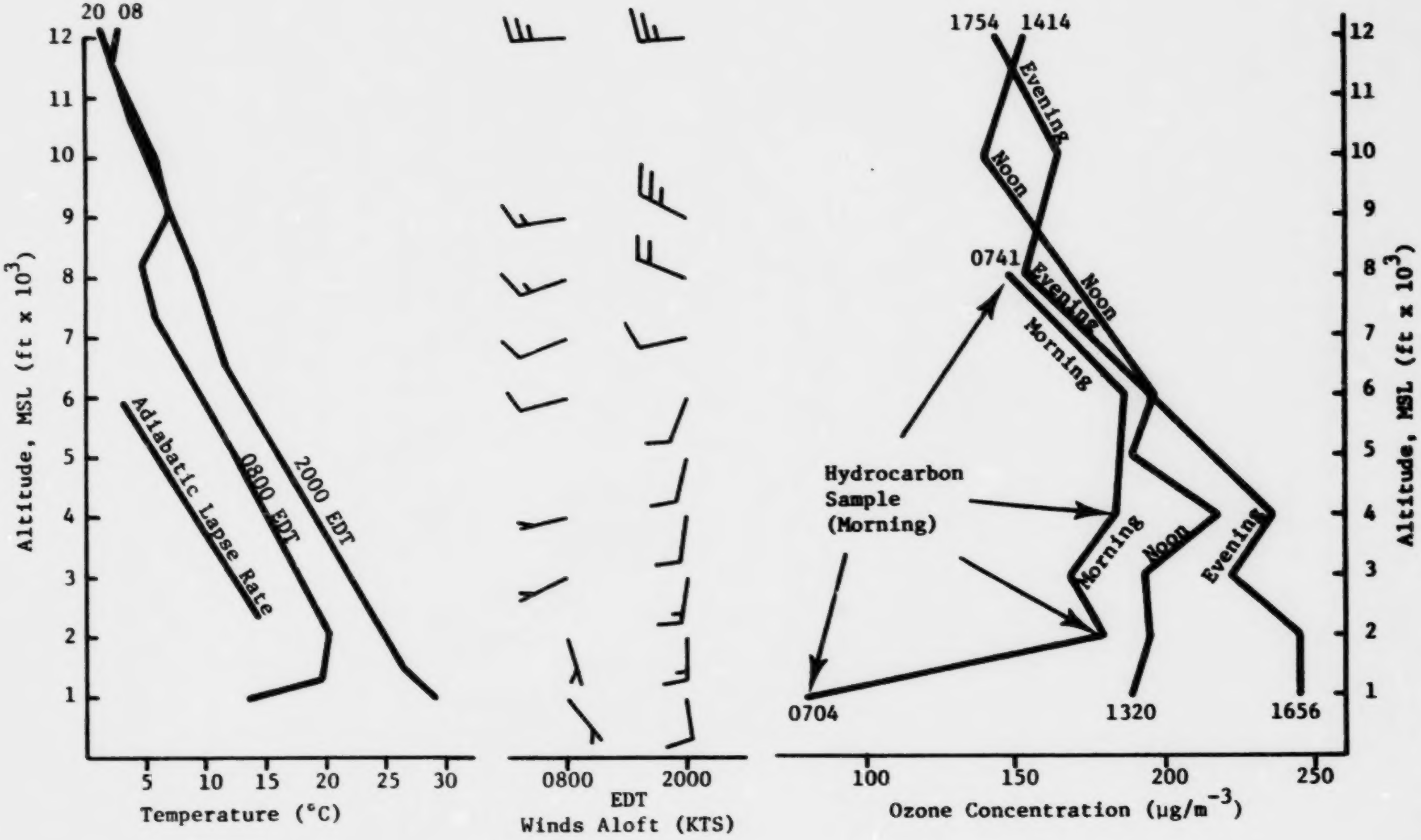


Figure 58. Ozone profile flight, Wilmington, Ohio, August 1, 1974.

Table 26. Abstract of hydrocarbon data: vertical profile flight Wilmington, Ohio, August 1, 1974

Category	Sampling altitude (meters) (Time-EDT)		
	Ground 0845- (0900 am)	Ground 1210- (1315 pm)	609.6 m (0715 am)
Ozone, $\mu g/m^3$	30.	110.	179.
Acetylene, ppbc	3.8	0.9	1.4
Acetaldehyde/acetylene	1.4	3.2	1.1
Carbon monoxide, ppm	0.28	0.17	0.22
Carbon monoxide/acetylene	74.	189.	157.
Isobutylene/isobutane	0.4	1.0	0.1
Propylene/propane	0.3	0.5	0.3
Ethylbenzene/acetylene	0.2	1.2	0.2
Propylene/acetylene	0.4	0.2	0.4

	1219.2 m (0730 am)	2438.4 m (0745 am)	2438.4 m (0750 am)
Ozone, $\mu g/m^3$	183.	128.	-
Acetylene, ppbc	1.4	0.4	0.4
Acetaldehyde/acetylene	1.7	5.0	6.3
Carbon monoxide, ppm	0.23	0.17	0.19
Carbon monoxide/acetylene	164.	425.	475.
Isobutylene/isobutane	0.1	0.1	2.3
Propylene/propane	0.2	0.5	0.6
Ethylbenzene/acetylene	0.1	0.3	0.3
Propylene/acetylene	0.3	1.3	1.5

Table 27. Abstract of hydrocarbon data: vertical profile flight Wooster and McConnelsville, Ohio, August 13, 1974

Category	Sampling altitude (meters) (Time-EDT)			
	Wooster			
	Ground (~1130 am)	762 m (1157 am)	1524 m (1146 am)	2286 m (1135 am)
Ozone, µg/m^3	142.	151.	125.	121.
Acetylene, ppbc	2.2	1.5	0.3	0.2
Acetaldehyde/acetylene	1.6	3.3	11.3	16.5
Carbon monoxide, ppm	0.4	-	-	-
Carbon monoxide/acetylene	168.	-	-	-
Isobutylene/isobutane	2.2	>0.2	0.4	0.5
Propylene/propane	0.2	0.9	0.1	0.2
Ethylbenzene/acetylene	0.4	0.3	0.7	1.0
Propylene/acetylene	0.6	0.5	1.0	0.2

	McConnelsville			
	Ground (~1230 pm)	762 m (1313 pm)	1524 m (1303 pm)	2286 m (1252 pm)
Ozone, µg/m^3	149.	153.	121.	111.
Acetylene, ppbc	2.0	1.6	0.6	0.4
Acetaldehyde/acetylene	1.5	2.0	3.0	6.5
Carbon monoxide, ppm	0.3	-	-	-
Carbon monoxide/acetylene	160.	-	-	-
Isobutylene/isobutane	0.2	>0.1	0.7	3.5
Propylene/propane	0.1	0.1	0.1	0.5
Ethylbenzene/acetylene	0.3	0.1	0.3	-
Propylene/acetylene	0.5	0.5	1.0	4.3

Table 28. Abstract of hydrocarbon data: vertical profile flight Wilmington, Ohio, August 15, 1974

Category	Sampling altitude (meters) (Time-EDT)						
	Ground (~1130 am)	610 m (1056 am)	1220 m (1121 am)	1830 m (1134 am)	2490 m (1158 am)	3050 m (1208 am)	3660 m (1220 pm)
Ozone, μg/m^3	117.	160.	186.	124.	109.	70.	90.
Acetylene, ppbc	2.7	2.7	1.7	3.4	0.2	0.2	>0.1
Acetaldehyde/acetylene	1.1	1.2	2.3	0.7	16.	11.	>11.
Carbon monoxide, ppm	0.58	0.59	0.31	0.80	0.14	0.13	0.14
Carbon monoxide/acetylene	215.	219.	182.	235.	700.	650.	>1400.
Isobutylene/isobutane	0.1	0.1	0.3	0.2	0.5	4.3	-
Propylene/propane	0.1	0.1	0.2	0.7	0.4	0.8	1.9
Ethylbenzene/acetylene	0.4	1.3	0.2	0.2	0.5	0.	1.0
Propylene/acetylene	0.2	0.2	0.4	0.1	3.5	10.	21.

was probably due to some movement of ozone upward from the mixing layer into air which probably had no ozone synthesis or, at best, a minimal generation.

The series of three vertical flights made on August 1 (figure 58) indicate some photochemical ozone generation by the time of the "noon" samples. By the time of the "evening" samples, the ozone concentration at the ground had equalled or slightly exceeded the samples taken at 610 m (2000 ft) to 1220 m (4000 ft) and all concentrations measured at or below 1220 m (4000 ft) were higher than the morning concentrations.

The hydrocarbon analyses show a general althcugh not universal tendency for acetylene to decrease with increasing altitude. At some point aloft, however, the acetylene concentrations dropped precipitously, as for example at 2440 m (8000 ft) on August 5 and August 15 over Wilmington, and 1525 m (5000 ft) over Wooster and McConnelsville on August 13. The acetaldehyde/acetylene and the propylene/acetylene ratios increased many fold at the same time. Supposedly, however, the acetylene is less reactive in atmospheric oxidation than other organics which are diluted along with acetylene, so that the hydrocarbon/acetylene ratio should furnish a measure of the extent of selective oxidation of the hydrocarbon. That the acetaldehyde/acetylene ratio aloft was several-fold larger than at lower levels (this was observed on all vertical flights) could be interpreted in one of two ways, if one considers acetylene as unreactive.

1. A longer time was available in the air aloft for conversion of hydrocarbons to aldehydes (or a faster rate of conversion occurred) than at lower elevations.

2. The air aloft, in which the acetaldehyde/acetylene ratios were startlingly greater than at lower elevations, had a completely different history from the air beneath it in terms of injection of pollutants.

A rational explanation for the increased propylene/acetylene ratio is not easily perceived unless the air aloft had a different history of pollutant injection from the air near the ground. Propylene should be destroyed more rapidly than acetylene, and its generation in the atmosphere from other organic compounds seems kinetically and mechanistically improbable. The propylene/acetylene phenomenon was observed on all vertical flights except the August 13 flight over Wooster.

6.1.5 Summary of Results Relating to Aircraft Flight

In making conclusions about the aircraft data, it is instructive to refer again to several tables and figures. Table 18 and figure 47 represent the square wave flight of July 21, 1974. The isobutylene/isobutane ratio should decrease steadily in a reaction chamber, even if it is being physically diluted. The same is true of the isopropylene/propane ratios. In the case of this flight, the C_4 ratio and the C_3 ratio were both 0.3 upwind of Columbus. Over Columbus the C_4 ratio was also 0.3, and the C_3 ratio was 0.4. In hydrocarbon sample 4 taken downwind of Columbus, both ratios were 0.6, indicating, at least, the injection of some olefins. The two samples taken over Dayton had C_4 ratios of 0.6 and 0.3 and C_3 ratios of 0.4 and 0.3. Sample 8 was taken at approximately the same point in space as sample 4. The ratios here were: sample 4, C_4; 0.6, C_3; 0.6; and sample 8, C_4; 0.3, C_3; 0.4. The time differential between samples 4 and 8 was about 1 hour (1306-1410). The C_3 ratio comparison for samples 2 and 9 (which are also comparable spacially) was as follows: the isobutylene/isobutane ratio was 0.3 in sample 9 and 0.4 in sample 2. If there is a pattern in this, it is not one which would be consistent with the idea of a slug of pollution drifting, like a smog chamber without walls, downwind from Columbus. Pollution from the ground is assumed to be constantly mixed upward. Carbon monoxide concentrations behave as if the substance had been injected in the air over Columbus and was slowly diluted as the air drifted downwind. The sequence of carbon monoxide values were: upwind 0.24 ppm, over Columbus 0.37 (at 1235) and 0.33 (at 1419) then 0.30, 0.28, 0.26, 0.23, and 0.23 ppm. As the flight got further downwind from Columbus, the same kind of sequence can be seen in the acetylene concentration of the various samples.

Although there is clearly a region-wide (radius of 200 km [125 miles] or more) system of high ozone concentration, a strong inference can be made for the production of perturbations on the system (itself nonhomogeneous) by the cities in the form of "hot spots." A good example of the latter was found on the August 21 flight (fig. 57), which shows concentrations of ozone to the northwest of Pittsburgh (approximately 50 km (30 miles) downwind) ranging from 302 to 405 $\mu g/m^3$ with all adjacent readings on the flight path below 300 $\mu g/m^3$ and values approximately 40 km (25 miles) upwind of Pittsburgh with values ranging from about 150 to 280 $\mu g/m^3$. The acetylene concentration measured downwind of Pittsburgh was 6.9 ppbc as compared with a range of 1.3 to 2.8 ppbc in the rest of the flight samples.

On the double box flight of July 9 (figure 52 and table 21), the urban influence of Columbus is seen to extend at least 70 km (44 miles) to the east. This can be seen in both the hydrocarbon analyses and in the ozone concentrations. In the two samples taken over the city, acetylene concentrations are 3.8 and 3.5 ppbc, the concentrations north of the city (inner-box value first, then outer-box value) were 2.3 and 1.8; on the west they were 2.1 and 1.7; on the south they were 1.9 and 1.9; on the east the inner box concentration was 8.9 and the outer box 3.5 ppbc. The fact that the acetylene concentration of the eastern part of the inner box was greater than the over-the-city concentrations could be either a peculiarity of the plume distribution or representative of an earlier hour of greater urban activity. The same phenomenon can be observed when the ozone concentrations and the carbon monoxide concentrations in various parts of the flight pattern were compared. This latter case (i.e., the Columbus double box pattern) is clear cut, but the Pittsburgh influence (at about 50 km) inferred from the data of August 21 may have been due to some source other than Pittsburgh although no such source has been positively identified.

In figure 48, data for acetylene, isopentane, and carbon monoxide from the flight on Sunday, July 21, are plotted versus distance downwind of Columbus. In air measured downwind of Columbus, the elevation over concentrations measured upwind continued for about 69 km (43 miles) for acetylene, about 48 km (30 miles) for isopentane, and about 69 km (43 miles) for carbon monoxide. The concentration increased over the city. It varied somewhat downwind but remained elevated over the upwind concentration.

The overall patterns of hydrocarbon and ozone concentrations, though considerably irregular, suggests a trend toward an increase aloft over or slightly downwind of the city, followed at a further distance by a return to the background concentration plus, at times, a slight increment.

The data indicate an extent of urban influence which is detectable and assignable to a specific city if that city is about 80 km (50 miles) or less distant from the sampling point.

The nitric oxide and nitrogen dioxide concentrations aloft, except in rare cases, were undetectable with the instrument used. This instrument had been checked as to its proper operation at reduced pressures and was calibrated before each flight. Much smaller increases of ozone concentrations with increased time of solar irradiation, in spacially comparable samples, were measured aloft than either in the cities or at the non-urban surface stations. This plus the evidence from the vertical flights indicates that the diurnal curve of ozone concentrations above the radiation inversion layer is much shallower than that at the surface. The possibility exists that, at times, diurnal ozone trends aloft may be undetectable. The existance of a diurnal ozone trend aloft would be controlled by three things: the residue aloft of oxides of nitrogen and hydrocarbons left from the previous day, mixing of ozone precursors aloft and the mixing upward of ozone generated from fresh precursors emitted at the surface.

6.2 Interpretation of Ozone and Hydrocarbon Data from Ground Stations

6.2.1 Characteristics of Rural and Urban Ozone

Figures 59 and 60 show charts of the frequency distribution of the hour of occurrence of the daily maximum ozone concentration at each of the five rural and six urban stations during the summer of 1974. The chart in the lower righthand corner of each figure is the combined frequency distribution for the rural or urban stations. One station (Cincinnati) has been omitted from the set of combined urban station data because of the small number of observations.

Summary statistics for the daily maximum ozone concentration at each of the 11 stations are given in table 29. It is interesting to note that among the rural stations, only McHenry did not have a mean daily maximum ozone concentration value above the NAAQS. This is an unexpected result since McHenry, during the previous summer period of observation (1973), had ozone concentrations higher than those found at other stations in the area covered by the present study. None of the urban stations had mean daily maximum concentrations above the NAAQS. The lowest maximum daily ozone concentrations at all the rural stations were considerably higher than the corresponding concentrations at the urban stations.

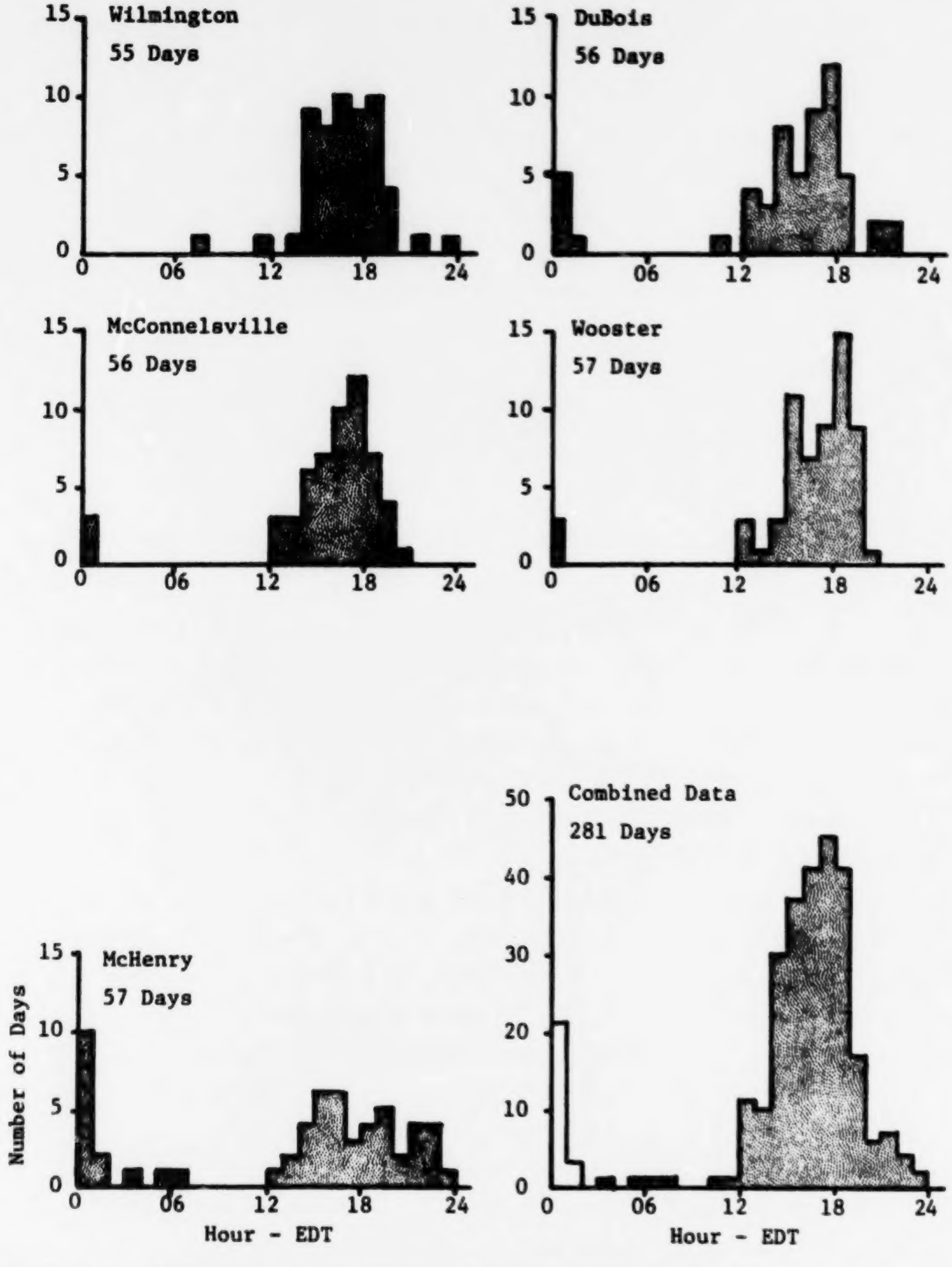


Figure 59. Frequency distribution of time of maximum hourly ozone concentrations at rural stations.

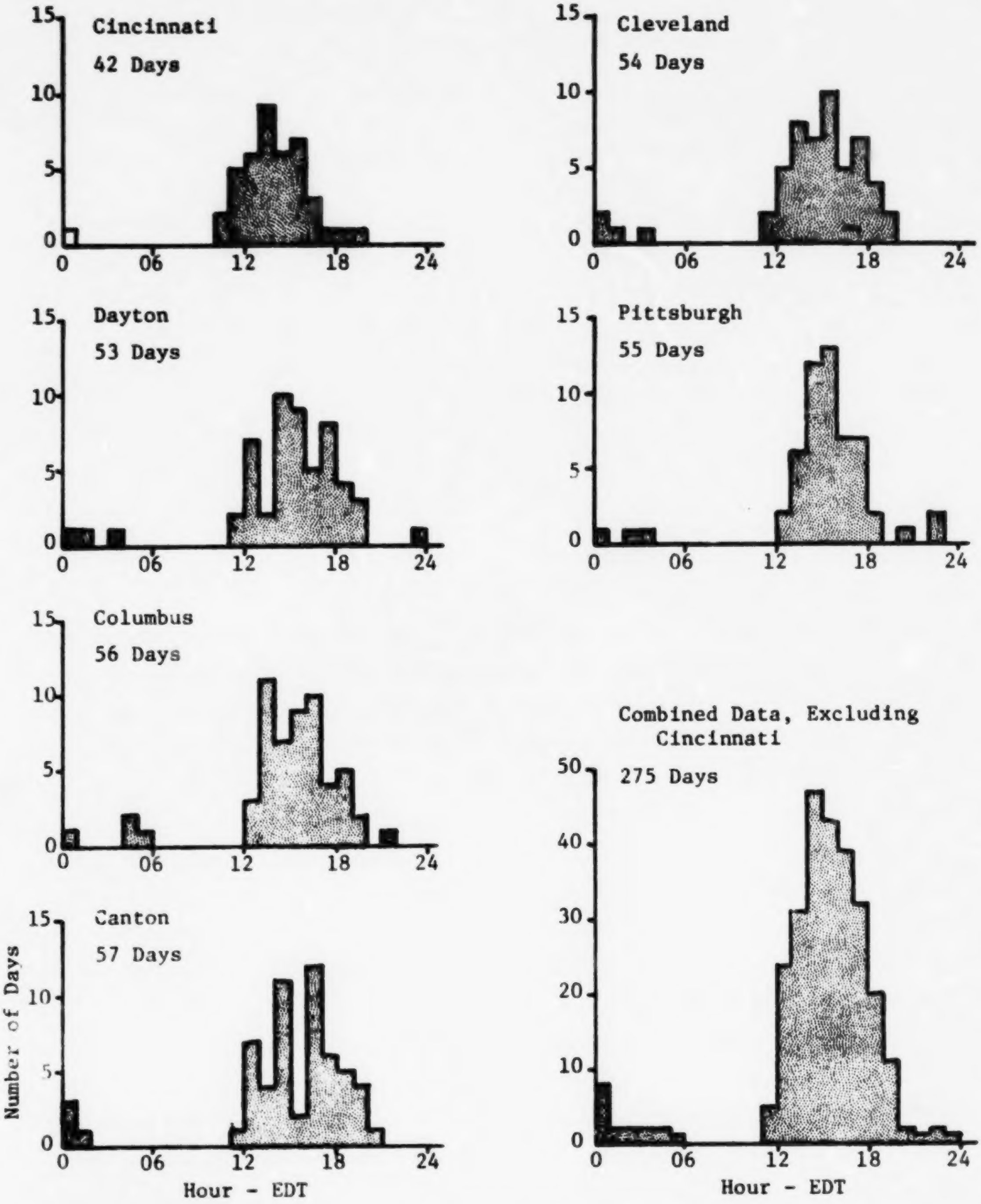


Figure 60. Frequency distribution of time of maximum hourly ozone concentrations at urban stations.

Table 29. Summary statistics for the daily maximum ozone concentration for five rural and six urban stations. The statistics are given in μg/m

	STATION										
	RURAL					URBAN					
Statistic	Wilmington	McConnelsville	Wooster	McHenry	DuBois	Cincinnati	Dayton	Columbus	Canton	Cleveland	Pittsburgh
Mean	187	171	183	158	187	140	151	158	158	135	149
Std. Dev.	54	43	54	55	65	60	44	67	51	51	56
Minimum	89	54	60	66	77	39	49	39	20	39	39
Maximum	370	330	330	330	400	360	260	340	280	270	308
No. of Days	55	56	57	57	56	42	53	56	47	54	55

Returning to the charts in figures 59 and 60, it is apparent that the individual station frequency distributions are not smooth functions, although for the most part, similar characteristics are displayed by both the rural and urban data. When the combined data charts for each of the two categories are compared, the similarity in the characteristics is more obvious. Both distributions are bimodal with the primary peak occurring in the late afternoon (not unexpectedly) and the secondary peak occurring in the hour after midnight. The most frequent times of occurrence of the ozone maximum concentrations in the two combined data sets show a difference of three hours; the rural maximum most frequently occurs during the hour between 1700 and 1800 EDT while the urban maximum occurs between 1400 and 1500 EDT. The greater number of occurrences of daily maximum ozone concentrations at the rural stations during the hour immediately following midnight may not be significant. Almost half of the occurrences in this hour at the rural stations are accounted for by McHenry data. This station may be unique among the group because of its hilltop location and the consequent potential (but not proven) advection of higher ozone concentrations from aloft as a result of nocturnal, katabatic wind flow.

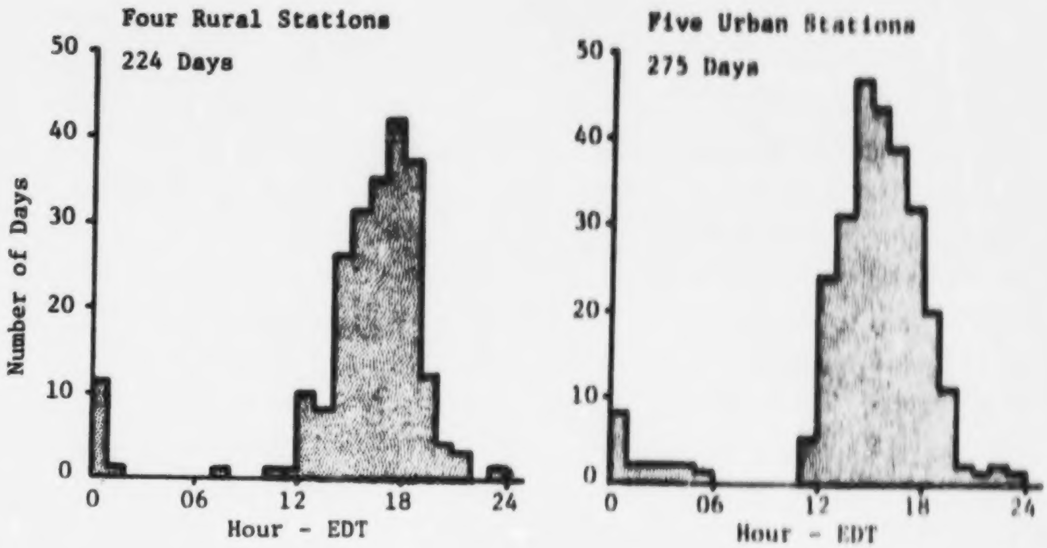


Figure 61. Comparison of frequency distribution of time of hourly maximum ozone for rural and urban stations.

If, on the basis of the above discussion, the McHenry data are eliminated, the frequencies of occurrence of the time of hourly maximum ozone concentrations for rural and urban stations compare as shown in figure 61. The general characteristics of the rural distribution have not changed. The maximum hourly ozone concentration is still indicated as being most frequently measured during the hour between 1700 and 1800 EDT at the rural stations, and the bimodal distribution is still apparent.

In summary, the data indicate that the maximum hourly ozone concentration usually occurs in both urban and rural areas between the hours of 1200 and 2000 EDT. The maximum hourly ozone concentration is lower in urban areas than in rural areas and occurs about three hours earlier. These features perhaps are related. If some "process" in the urban area, such as increased release of nitric oxide from afternoon automobile traffic, operates to counteract the increase in ozone anticipated as a result of photochemical reactions, the maximum concentration obtained would be lower and would occur earlier in time, relative to events in the absence of that "process." The process might involve an increase in emissions of nitric oxide associated with increases in traffic at a time in the day when ultraviolet irradiation is also declining. A similar effect of nitric oxide would not be prevalent in rural areas.

Since the pattern of the time variation of ozone concentration on a daily basis is determined not only by the maximum concentration values, but also by the minimum daily values, similar frequency distributions for the time of occurrence of the minimums are presented in figures 62 and 63. Again, data for the five rural and the six urban stations are shown individually but in the combined data sets Cincinnati (urban) has been omitted because of the shorter period of record.

Summary statistics for the distribution of daily minimum ozone concentrations at each of the 11 stations are given in table 30.

Table 30. Summary statistics for the daily minimum ozone concentration for five rural and six urban stations
(Except for the number of days, the statistics are given in μg/m^3.)

	STATION										
	RURAL					URBAN					
Statistic	Wilmington	McConnelsville	Wooster	McHenry	DuBois	Cincinnati	Dayton	Columbus	Canton	Cleveland	Pittsburgh
Mean	41	45	28	81	50	1	6	5	11	8	3
Std. Dev.	24	18	23	33	39	4	13	8	15	13	8
Minimum	1	7	0	30	0	0	0	0	0	0	0
Maximum	11	91	95	179	160	20	49	39	74	49	39
No. of Days	56	60	61	61	58	46	57	60	61	58	59

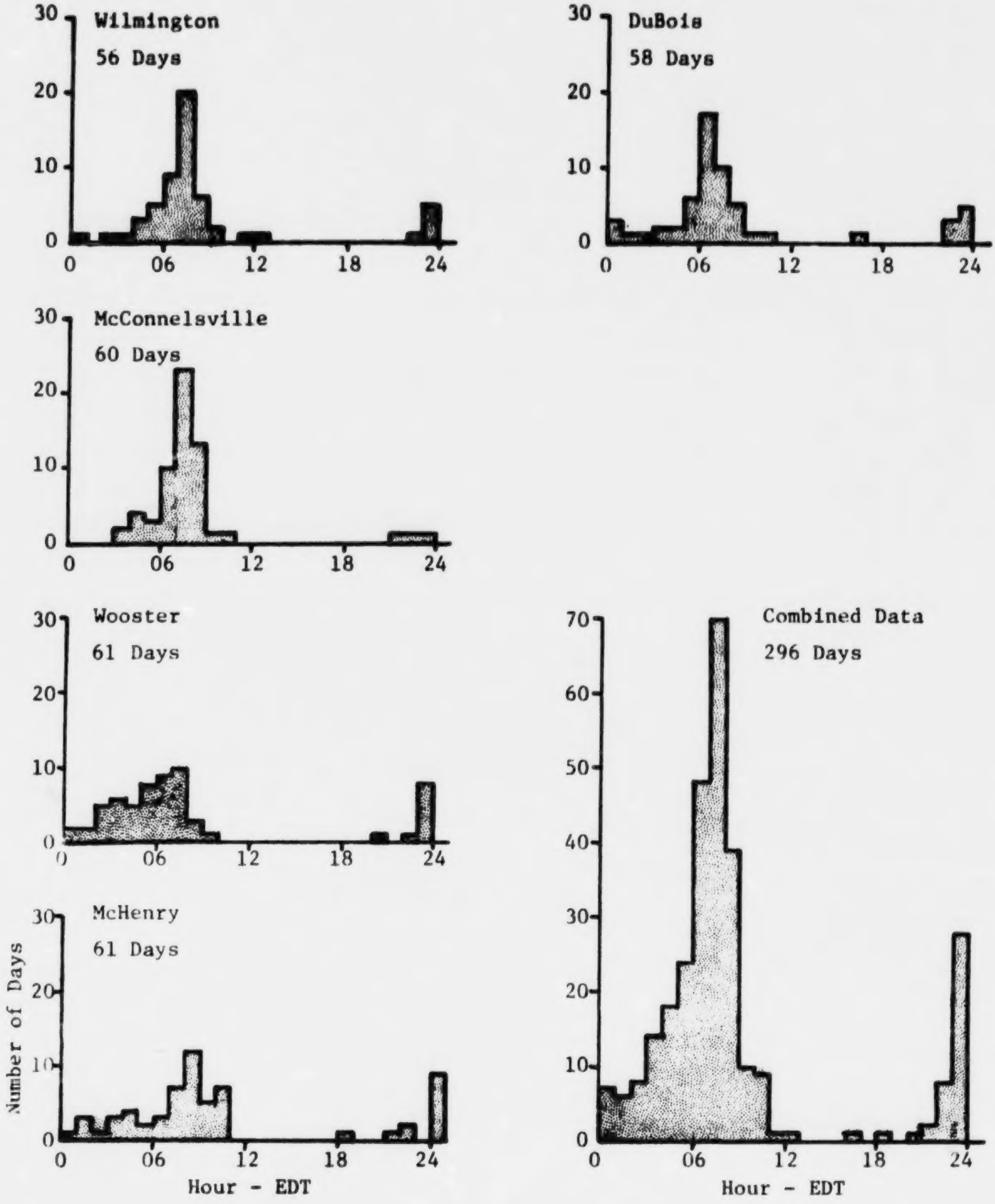


Figure 62. Frequency distributions of times of hourly minimum ozone concentrations for rural stations.

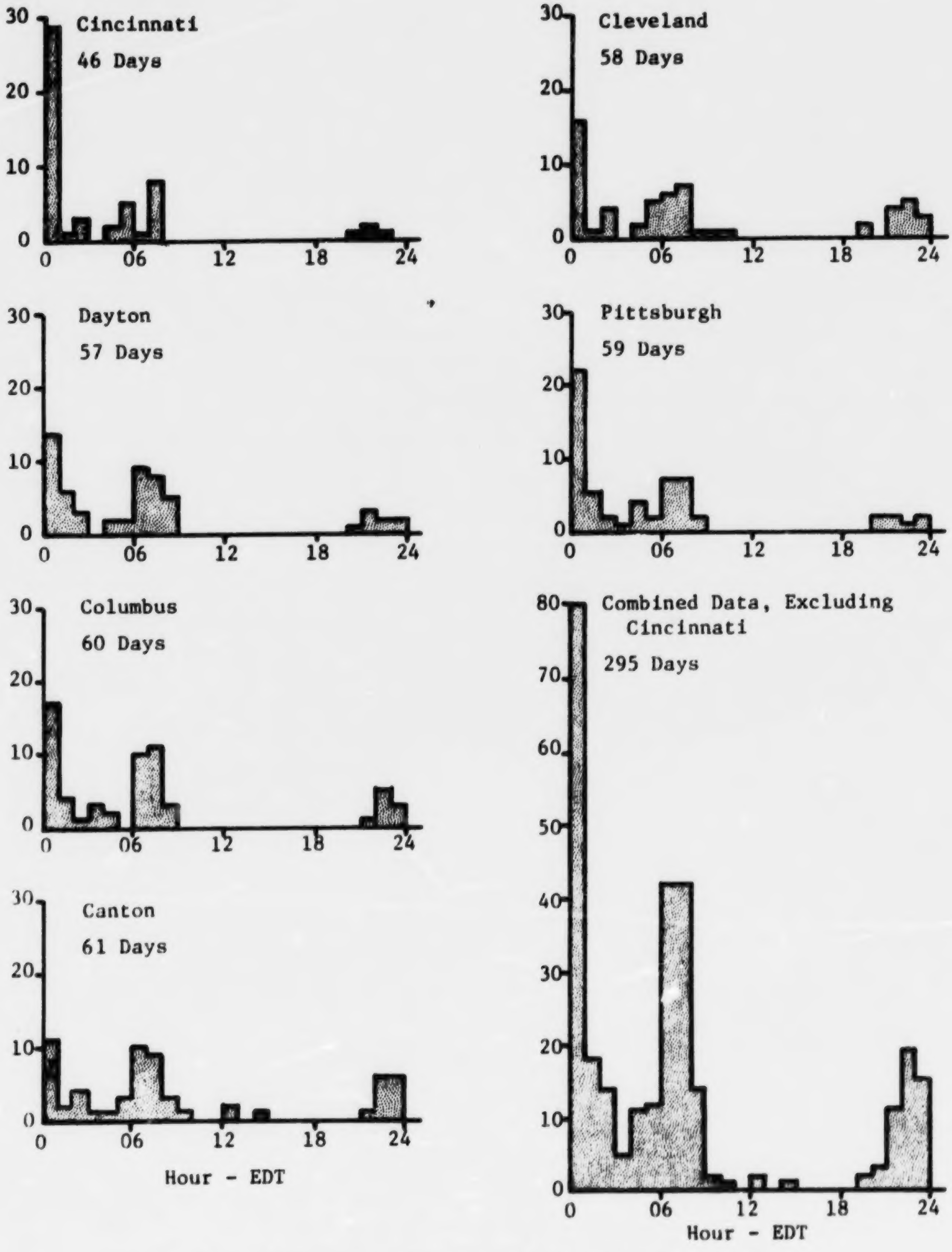


Figure 63. Frequency distributions of times of hourly minimum ozone concentrations for rural stations.

The higher mean minimum concentrations of ozone at the rural stations, compared to the urban stations, coupled with the fact that most (2/3) of the rural stations during this period did not experience a single 1-hour period of no measurable concentration of ozone, suggest that the ozone-destruction mechanisms in the rural areas are less active, or less effective, than in the urban areas. This may be accounted for, perhaps, by a greater abundance of nitrogen oxides from combustion sources in the urban air.

From the frequency distributions given in figures 62 and 63, and in particular from the combined data for the urban stations and for the rural stations (figure 64), certain common features are apparent. Both data sets have essentially bimodal frequency distributions, with peaks in the hours immediately following sunrise (0600 to 0900 EDT) and in the hours near midnight. A striking difference is evident, however, in the high number of occurrences of the daily minimum value of ozone concentration at the urban stations during the hour immediately following midnight EDT. At all urban stations the minimum value of ozone concentration occurred most frequently during this hour. In the absence of other data, this could be explained as a result of the occurrence of trends of increasing values of ozone concentration lasting over several-day periods--for example, during the first several days of the influence of high-pressure systems. Under such circumstances, assuming the upward trend of values was persistent, the first hour of each day would have the minimum ozone concentration for that day. However, since a similar high frequency of occurrence of the minimum during this hour did not occur at the rural stations, explanation of the basis of a trend of increasing concentrations is not tenable.

The occurrence of this peak in frequency of occurrence most likely is due to the procedure used in summarizing the data when the same minimum value of ozone concentration occurred during more than one hour during a day. This procedure called for crediting the earliest of the multiple hours with the event. In the case of urban data, the frequent occurrence of the limiting value of zero for ozone concentration precluded a time distribution of the minimum and increased the apparent frequency of occurrence during the first hour of the day.

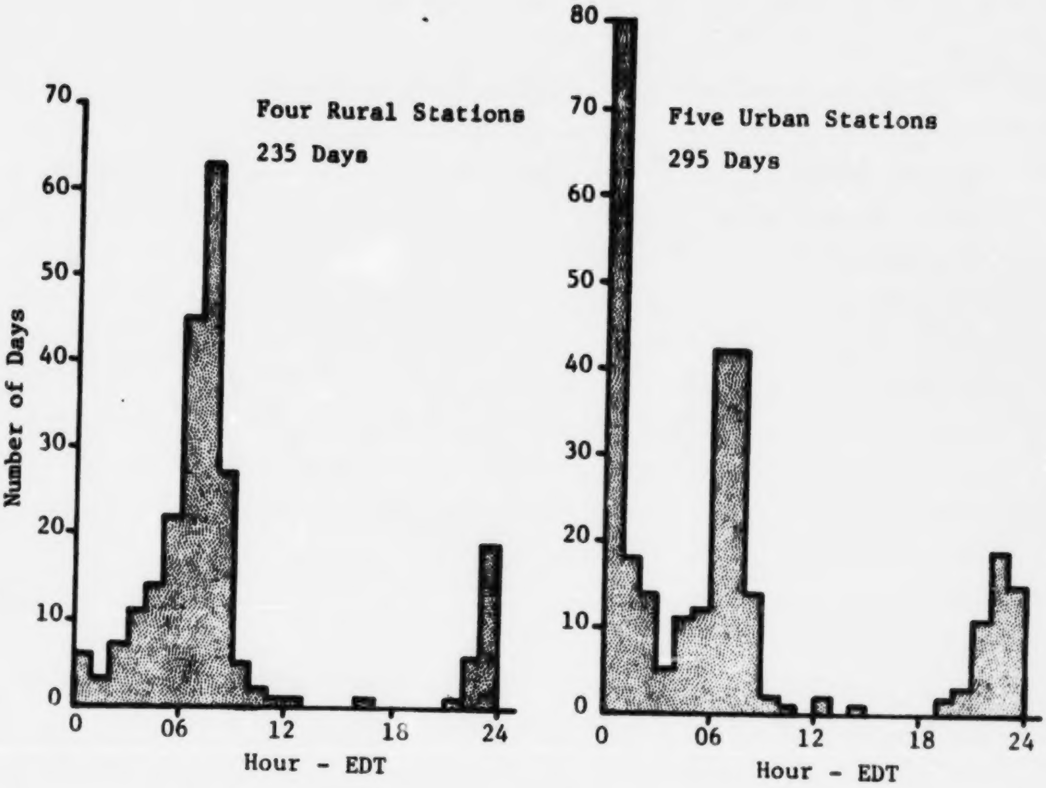


Figure 64. Comparison of frequency distributions of time of hourly minimum ozone concentrations for rural and urban stations.

6.2.2 Ozone and Hydrocarbon Data at Ground Stations

Examination of figures 31 and 32 shows that the diurnal ozone trends at the ground-based rural sites are well defined. The lowest hourly concentrations occurred usually in the 0800-0900 period. The concentration peaked around the 1700-1900 period and then exhibited an overall decrease throughout the night. Minima to maxima differentials on days of high ozone were of the order of 100 $\mu g/m^3$ or greater.

Three studies were made at Wilmington to examine diurnal variations of hydrocarbon concentrations. Times for collection of the other samples taken during the summer were separable into three periods--morning, noon, and evening. A comparison of the morning (0600-1000), noon (1000-1400), and evening (1400-1800) concentrations of acetylene and ozone from Wilmington, McConnelsville, and Wooster is presented in figure 65. The ozone concentrations were progressively larger as the day went on, whereas the acetylene concentrations were at a low in the noon samples. Acetylene concentrations in the evening samples were higher than the noon samples, indicating a fresh input of hydrocarbons. The low for acetylene at noon was probably related to two factors, a decrease in automobile traffic (over morning and evening), and a greater dilution due to mixing.

Diurnal Studies

Acetylene concentrations from three diurnal studies at Wilmington are plotted in figures 66, 67, and 68 along with the simultaneous ozone concentrations. Hydrocarbon concentrations and ratios from the diurnal studies are presented in tables 31, 32, and 33. The three sets of data seem to have come from three different systems or populations. The ozone and acetylene concentrations correlate directly on July 18 and inversely on July 23.

The July 23 case (fig. 67) can be explained in almost classical terms: high hydrocarbon, low ozone at the time of maximum traffic, maximum ozone, minimum hydrocarbon, slightly after midday (a function of photochemistry and traffic patterns), and a decay of ozone concentrations and a buildup of hydrocarbons in the nocturnal radiation inversion layer. There was an influx of acetylene in the 1400 to 1600 sample inferred to be the influence of noon-time auto traffic at some point upwind. The 1400 to 1600

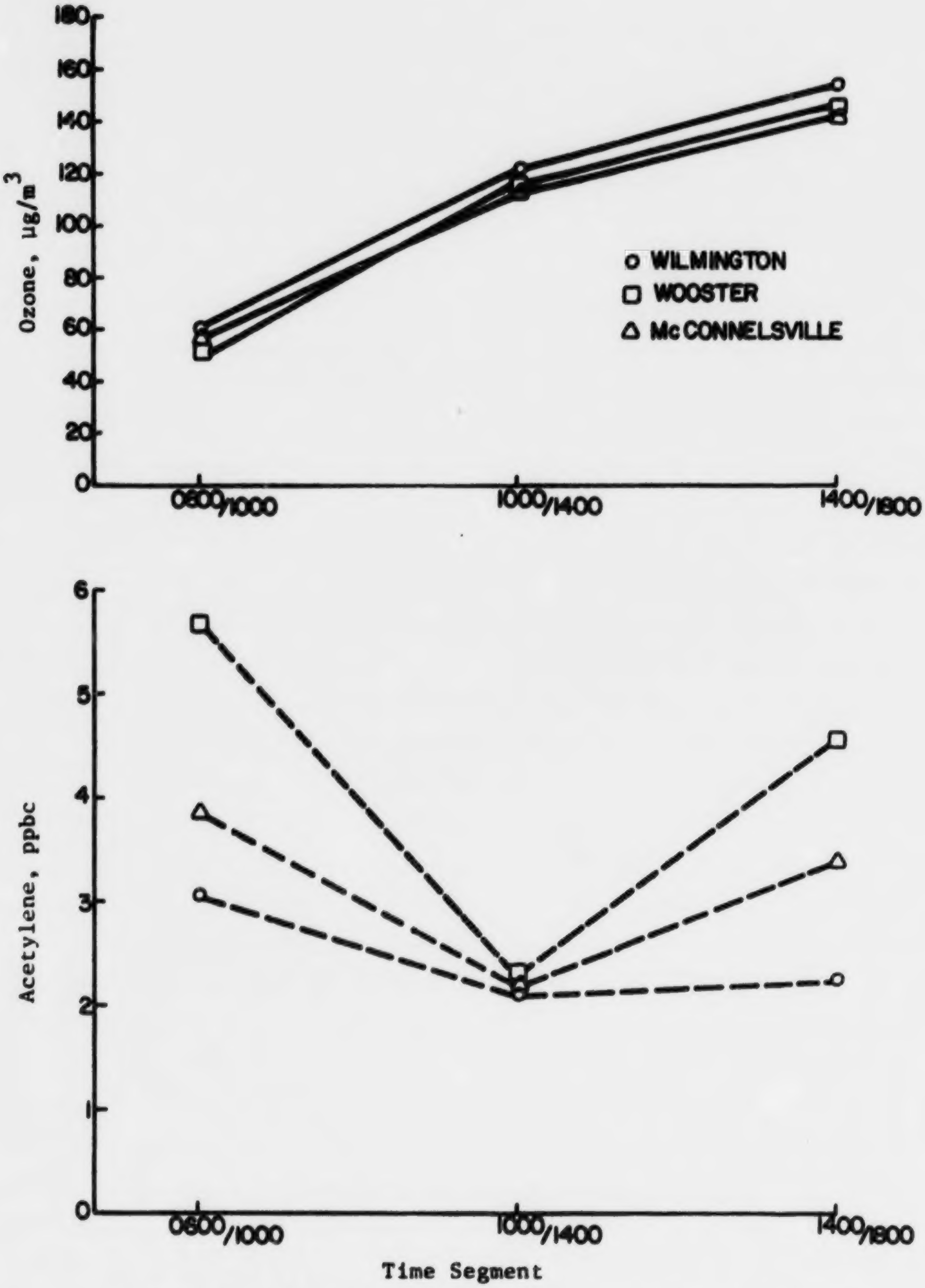


Figure 65. Variation of ozone and acetylene with time of day, Ohio ground stations.

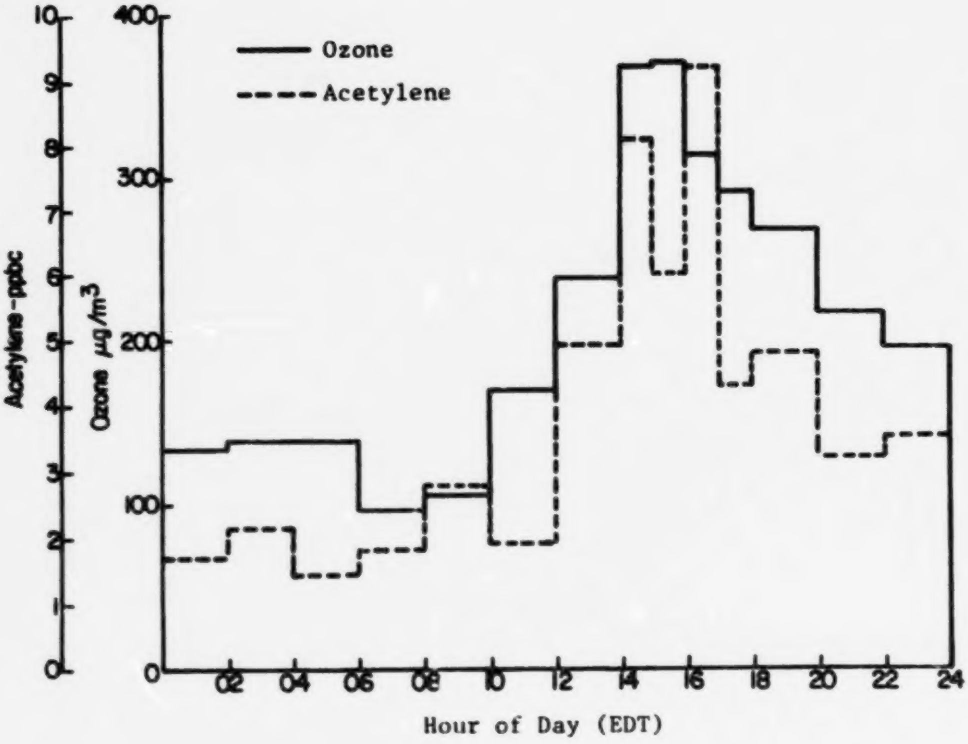


Figure 66. Acetylene and ozone variations. Diurnal study, Wilmington, Ohio, July 18, 1974.

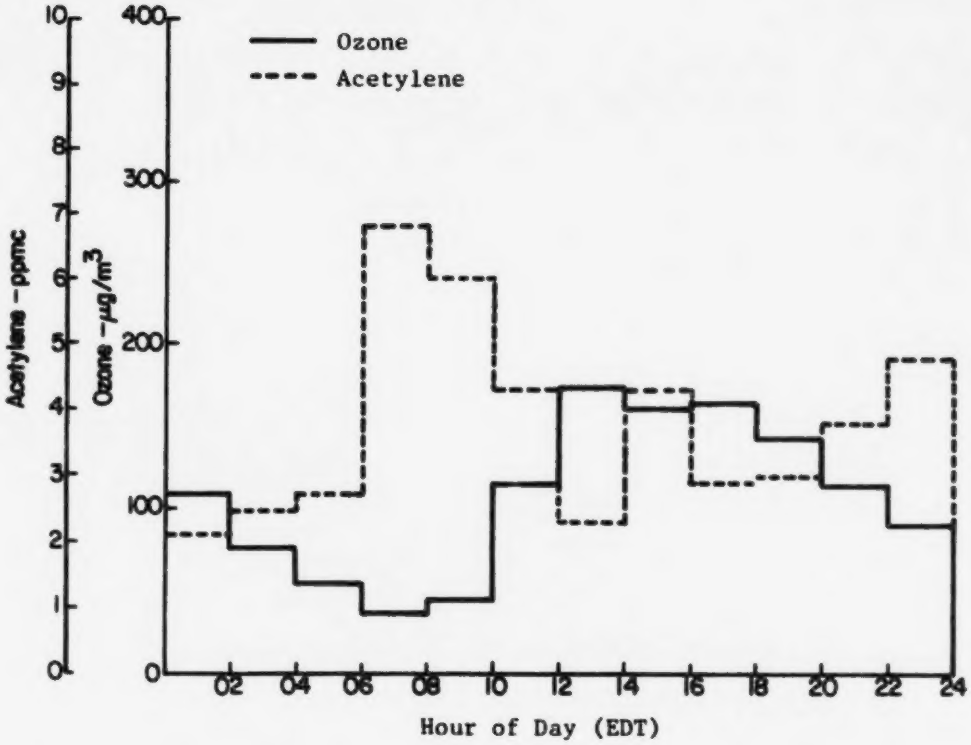


Figure 67. Acetylene and ozone variations. Diurnal study, Wilmington, Ohio, July 23, 1974.

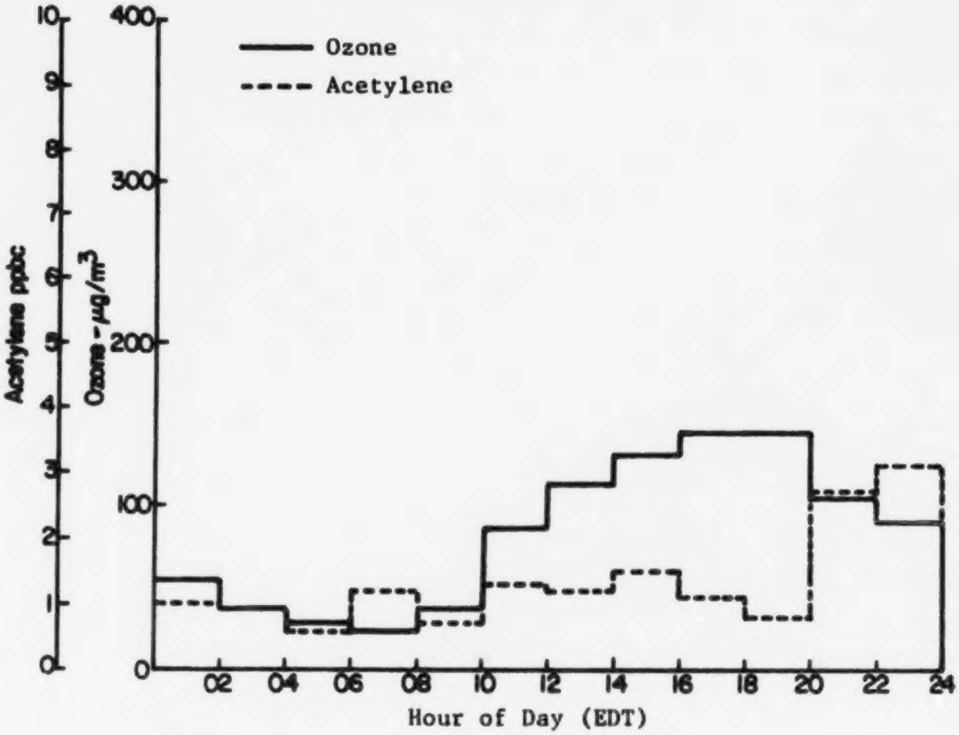


Figure 68. Acetylene and ozone variations. Diurnal study, Wilmington, Ohio, August 14, 1974.

Table 31. Abstract of hydrocarbon data: Diurnal study Wilmington, Ohio, July 18, 1974

Category	Time of sample collection (EDT)													
	0-2	2-4	4-6	6-8	8-10	10-12	12-14	14-15	15-16	16-17	17-18	18-20	20-22	22-24
Ozone, $\mu g/m^3$	132.	137.	138.	98.	106.	169.	240.	368.	369.	312.	285.	266.	218.	193.
Acetylene, ppbc	1.7	2.1	1.4	1.8	2.8	1.9	4.9	8.1	6.0	9.2	4.3	4.8	3.2	3.5
Acetaldehyde/acetylene	.1	.9	2.1	2.2	1.0	.7	.8	.8	1.3	.8	1.6	1.1	1.3	1.2
Carbon monoxide, ppm	.17	.18	.20	.20	.35	.31	.42	.68	.57	.59	.38	.43	.34	.34
Carbon monoxide/acetylene	100.	86.	143.	111.	125.	163.	86.	84.	95.	64.	88.	90.	106.	97.
Isobutylene/isobutane	.4	.4	.0	.5	.5	.3	.4	.0	.1	.4	.1	.1	.2	.2
Propylene/propane	.2	.1	.1	.1	.5	.1	.1	.1	.0	.2	.1	.1	.0	.1
Ethylbenzene/acetylene	1.1	.3	.3	.2	.3	.2	.1	.1	.1	.1	.1	.1	.1	.1
Propylene/acetylene	.4	.2	.4	.3	1.2	.4	.1	.1	.1	.1	.1	.1	.2	.2
Acetaldehyde, ppbc	2.0	1.8	2.9	3.9	2.9	1.3	3.8	6.7	7.5	7.3	7.0	5.1	4.1	4.3
Acetone, ppbc	4.5	5.0	1.7	6.9	4.5	3.0	6.4	19.2	20.7	11.1	9.3	11.4	6.7	6.0

Table 32. Abstract of hydrocarbon data: Diurnal study Wilmington, Ohio, July 23, 1974

	Time of sample collection (EDT)											
Category	0-2	2-4	4-6	6-8	8-10	10-12	12-14	14-16	16-18	18-20	20-22	22-24
Ozone, μg/m^3	101.	76.	56.	38.	42.	113.	168.	160.	163.	142.	115.	91.
Acetylene, ppbc	2.1	2.4	2.7	6.8	6.0	4.3	2.3	4.4	2.9	3.0	3.8	4.8
Acetaldehyde/acetylene	2.0	1.8	1.6	.7	.7	.8	1.1	1.0	2.7	1.8	1.3	2.7
Carbon monoxide, ppm	.29	.29	.28	.45	.44	.34	-	.43	.63	.40	.38	.40
Carbon monoxide/ acetylene	138.	121.	104.	66.	73.	79.	-	98.	217.	133.	100.	83.
Isobutylene/isobutane	.3	.2	.2	.3	.3	.2	.2	.2	.2	.2	.4	.3
Propylene/propane	.1	.1	.1	.1	.2	.1	.1	.1	.1	.2	.2	.2
Ethylbenzene/acetylene	>.5	.1	.2	.3	.2	.4	>.2	.2	.6	.7	.2	.2
Propylene/acetylene	.5	.5	.5	.4	.4	.3	.2	.2	.3	.6	.6	.4
Acetaldehyde, ppbc	4.2	4.2	4.3	4.5	4.4	3.5	2.6	4.6	7.8	5.4	5.1	12.8
Acetone, ppbc	4.7	9.7	19.7	11.5	10.2	8.0	6.9	9.2	-	4.9	8.6	12.5

Table 33. Abstract of hydrocarbon data: Diurnal study Wilmington, Ohio, August 14, 1974

Category	Time of sample collection (EDT)					
	0-2	2-4	4-6	6-8	8-10	10-12
Ozone, µg/m^3	55.	39.	29.	24.	39.	86.
Acetylene, ppbc	1.0	.9	.6	1.2	.7	1.3
Acetaldehyde/acetylene	2.1	1.8	2.7	1.2	3.3	2.2
Carbon monoxide, ppm	.13	.13	.13	.14	.16	.22
Carbon monoxide/acetylene	130.	144.	217.	117.	229.	169.
Isobutylene/isobutane	.36	.3	.3	.3	.3	.3
Propylene/propane	.2	.2	.2	.3	.1	.1
Ethylbenzene/acetylene	.9	.4	.7	.4	.4	.6
Propylene/acetylene	.7	.8	1.2	.5	.4	.3
Acetaldehyde	2.1	1.6	1.6	1.4	2.3	2.9
Acetone	3.1	2.3	2.0	2.4	1.0	2.0

	12-14	14-16	16-18	18-20	20-22	22-24
Ozone, µg/m^3	113.	131.	144.	142.	105.	91.
Acetylene, ppbc	1.2	1.5	1.1	0.8	2.7	3.1
Acetaldehyde/acetylene	1.5	1.4	2.1	2.7	1.0	0.8
Carbon monoxide, ppm	.18	.21	.21	.25	.31	.43
Carbon monoxide/acetylene	150.	140.	191.	313.	115.	139.
Isobutylene/isobutane	.2	.2	.4	.4	.5	.3
Propylene/propane	0	.1	.2	.2	.4	.2
Ethylbenzene/acetylene	.3	.3	.3	.6	.3	.4
Propylene/acetylene	0	.3	.5	.6	.4	.4
Acetaldehyde	1.8	2.1	2.3	2.2	2.8	2.5
Acetone	4.4	6.3	7.5	4.1	5.0	2.2

ozone concentration seems to have been prevented from reaching a potentially higher concentration due to injection of oxides of nitrogen into the air at the same time as the hydrocarbons. The July 18 case presents almost a complete reversal of the acetylene/ozone relationship as was depicted in the July 23 case. The unsatisfactory and tentative conclusion here is that vagaries of meteorology and transport must be evoked to explain this case. In the August 14 case (fig. 68) the acetylene concentrations were low and were virtually constant from 0000 to 2000 and the ozone showed a diurnal curve typical of others taken at this station.

The relationship of the hydrocarbons concentration to ozone concentration in this study can best be shown by figures 69 and 70. These figures should be considered as proof of the important involvement of anthropogenic pollution in the generation of the high ozone concentrations. High ozone concentrations were associated with relatively high acetylene concentration. If acetylene is only an anthropogenic and if some of the high ozone had been generated from natural precursors only, some of the high ozone concentrations should have occurred at the low end of the acetylene concentration. This should be a telling relationship for determining the participation of city air in the generation of rural ozone.

6.3 Relationship Between High Ozone Episodes and Synoptic Weather Conditions

6.3.1 Introduction

Recently, the literature has contained a number of studies in which the presence of high ozone (ozone concentrations greater than 160 $\mu g/m^3$) has been observed in rural boundary layers[3,11,12]. Miller et al.[11] have attributed the high ozone concentrations found in rural areas to the formation of ozone by anthropogenic precursors such as hydrocarbons and nitrogen oxides emitted from urban regions and transported to rural regions. However, Stasiuk and Coffey[12] have questioned this mechanism, but suggested no alternative. Bruntz et al.[13] have shown that the concentration of ozone is correlated to solar radiation and to wind speed. They have shown that the concentrations are lower with low levels of solar radiation (suggesting synthesis as the source of the high ozone) and also with high wind speeds.

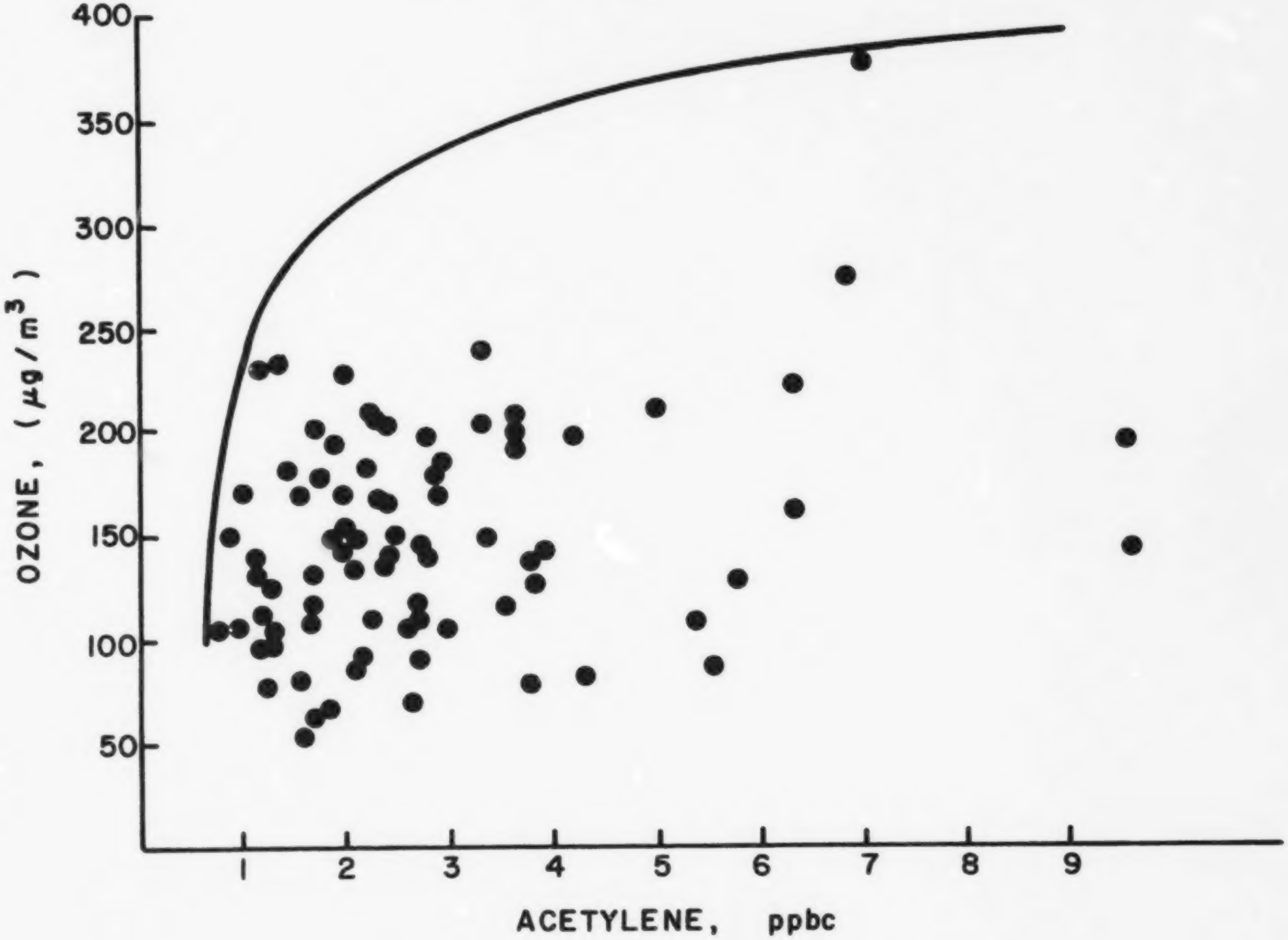


Figure 69. "Maximum Effect" curve (Ground Station Data).

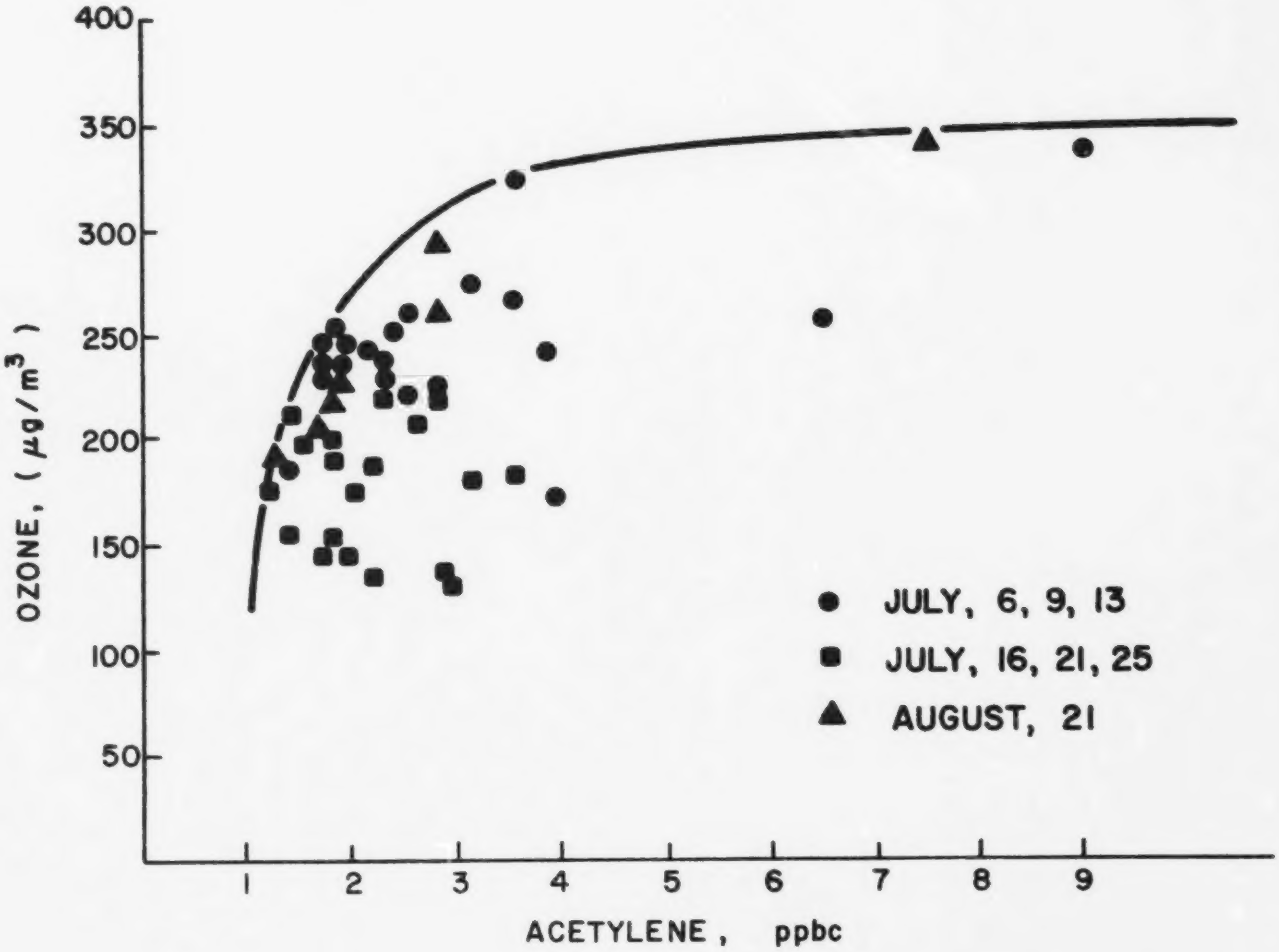


Figure 70. "Maximum Effect" curve (Aircraft Data).

Data collected by RTI in the summers of 1973 and 1974 have indicated that systemic increases of the ozone concentration over large areas often occur during this period. The data were collected by RTI in the eastern part of the United States at various stations placed in rural regions. This portion of the report summarizes some initial studies on the nature of the large-scale meteorological conditions at the surface when systemic, high ozone concentrations were found.

6.3.2 Correlation Between Pressure Systems and High Ozone

Figures 71 and 72 summarize the correlation found between high ozone concentrations and synoptic pressure systems. The ozone data presented in the graphs for each day represent the area average value of the maximum 1-hour average ozone concentrations observed at each station. The area average was constructed by averaging over all stations. The area averaged maximum concentration is employed in order to remove local anomalies which may exist at a given time and given station, and to demonstrate the systematic nature of the increases and decreases in ozone over a fairly large area (the maximum distance between stations was 480 kilometers). The pressure for each day is the area average station pressure for the region of interest.

These data indicate that high ozone concentrations are found when a high-pressure system exists in the region. The correlation is not one-to-one with respect to pressure; i.e., the highest pressure does not correlate with the highest ozone concentration and the lowest pressure does not correlate with the lowest ozone concentration. This is primarily due to the fact that pressure in itself does not affect ozone synthesis or the vertical mixing of ozone, which are the only mechanisms for increasing the ozone, nor does pressure affect the destruction of ozone. In terms of high ozone, it appears that high-pressure systems provide those environmental conditions that allow the production of high ozone.

Figures 73 and 74 show the result of computing a nine-point running mean using the same data employed to construct figures 71 and 72. The effect of computing running means is to filter out short-period synoptic fluctuations, leaving only the long-period trends. It is noted from

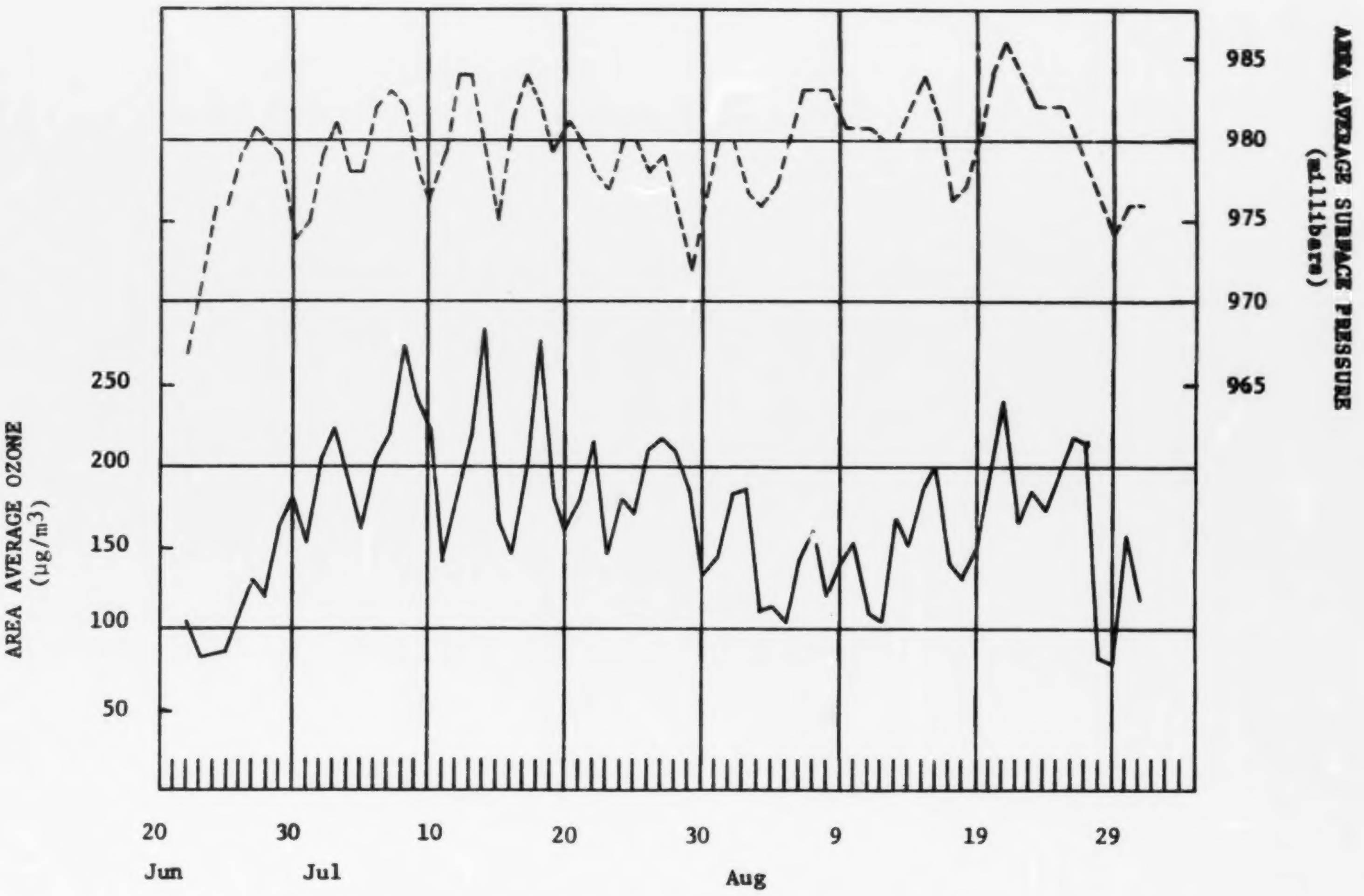


Figure 71. The area average value of the maximum ozone concentration (solid line) and the area average surface pressure (dashed line) versus day of the month for the later part of the summer 1974. (See Text)

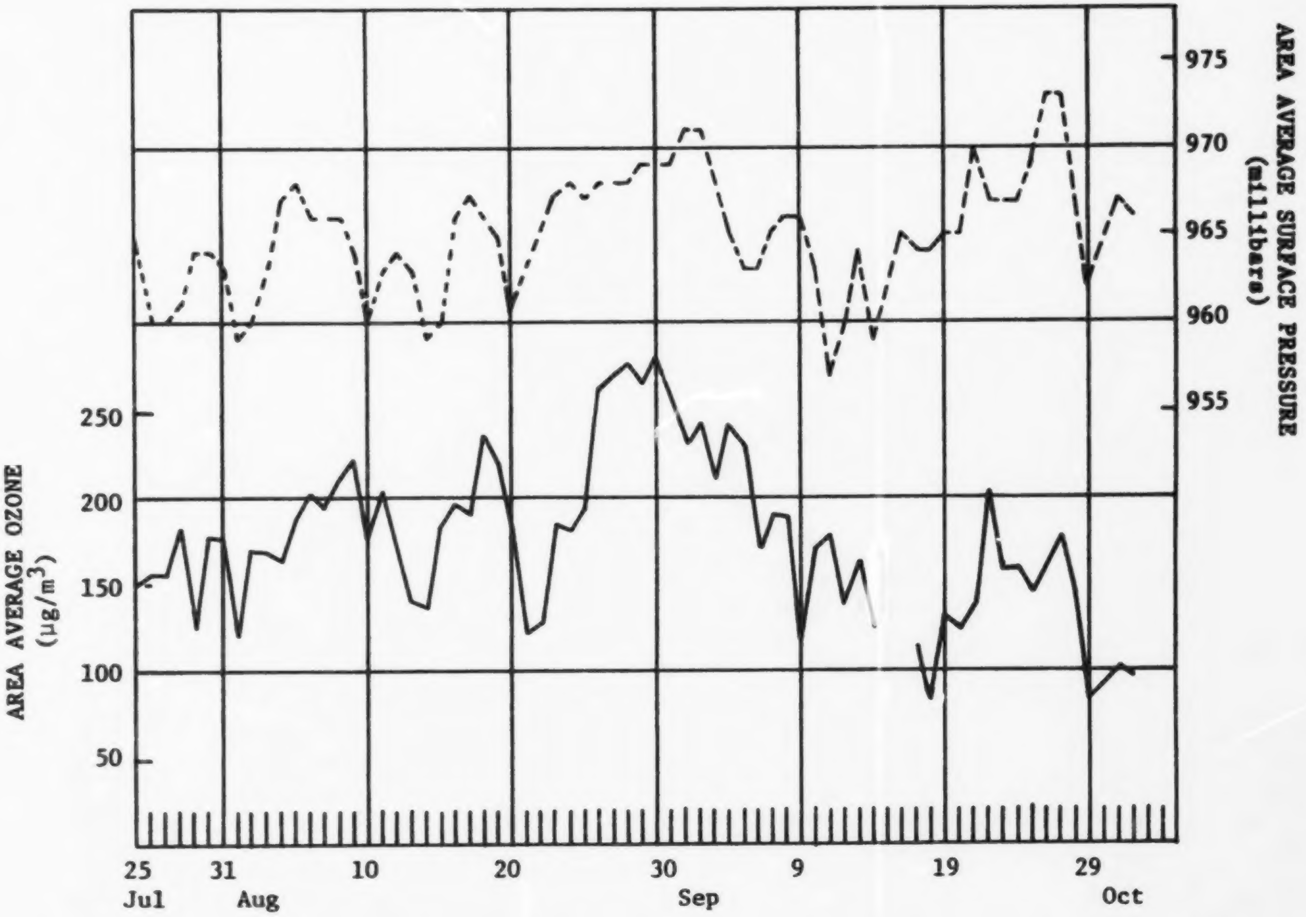


Figure 72. The area average value of the maximum ozone concentration (solid line) and the area average surface pressure (dashed line) versus day of the month for the latter part of the summer 1973.

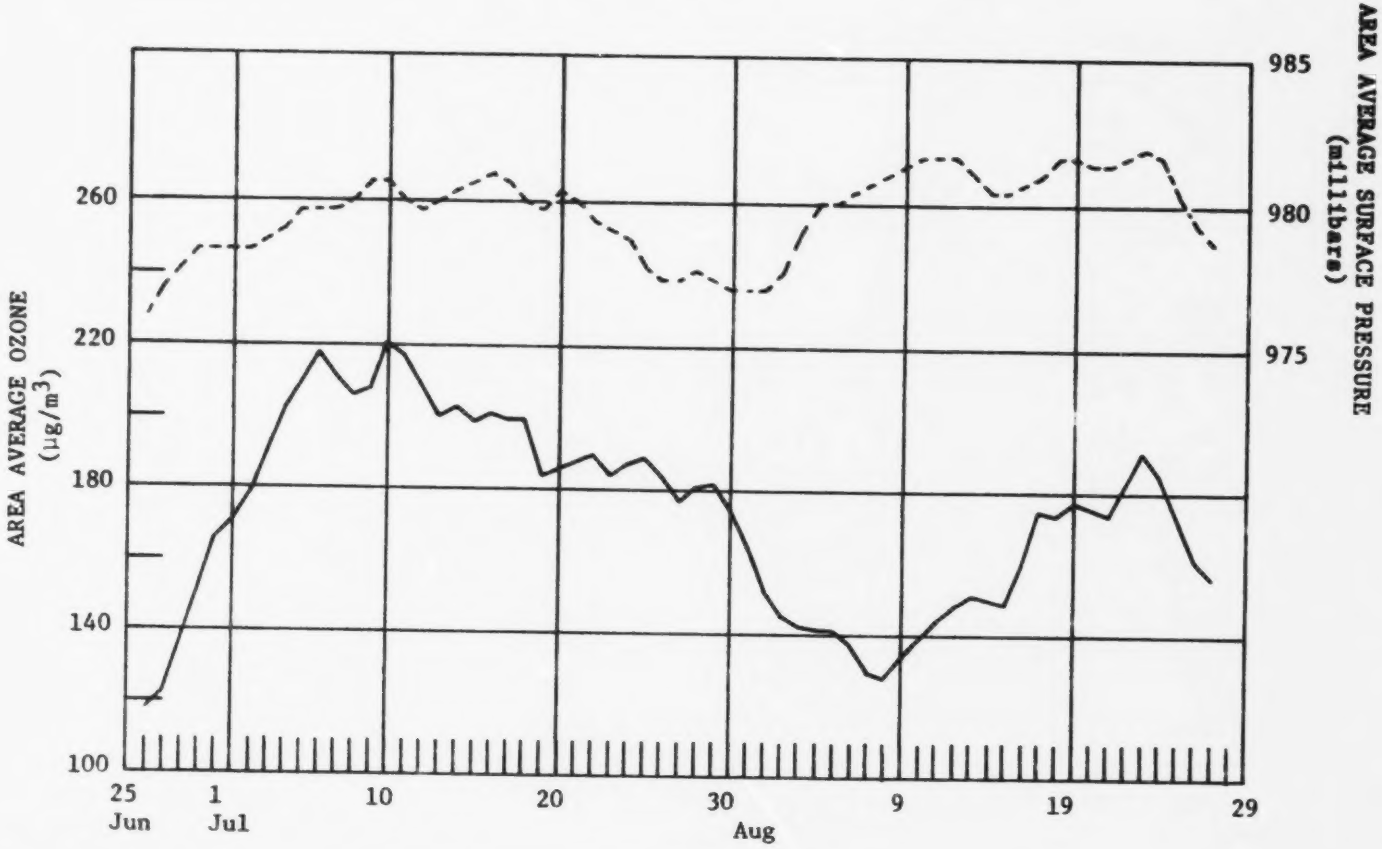


Figure 73. Nine-point running average of the data presented in figure 71.

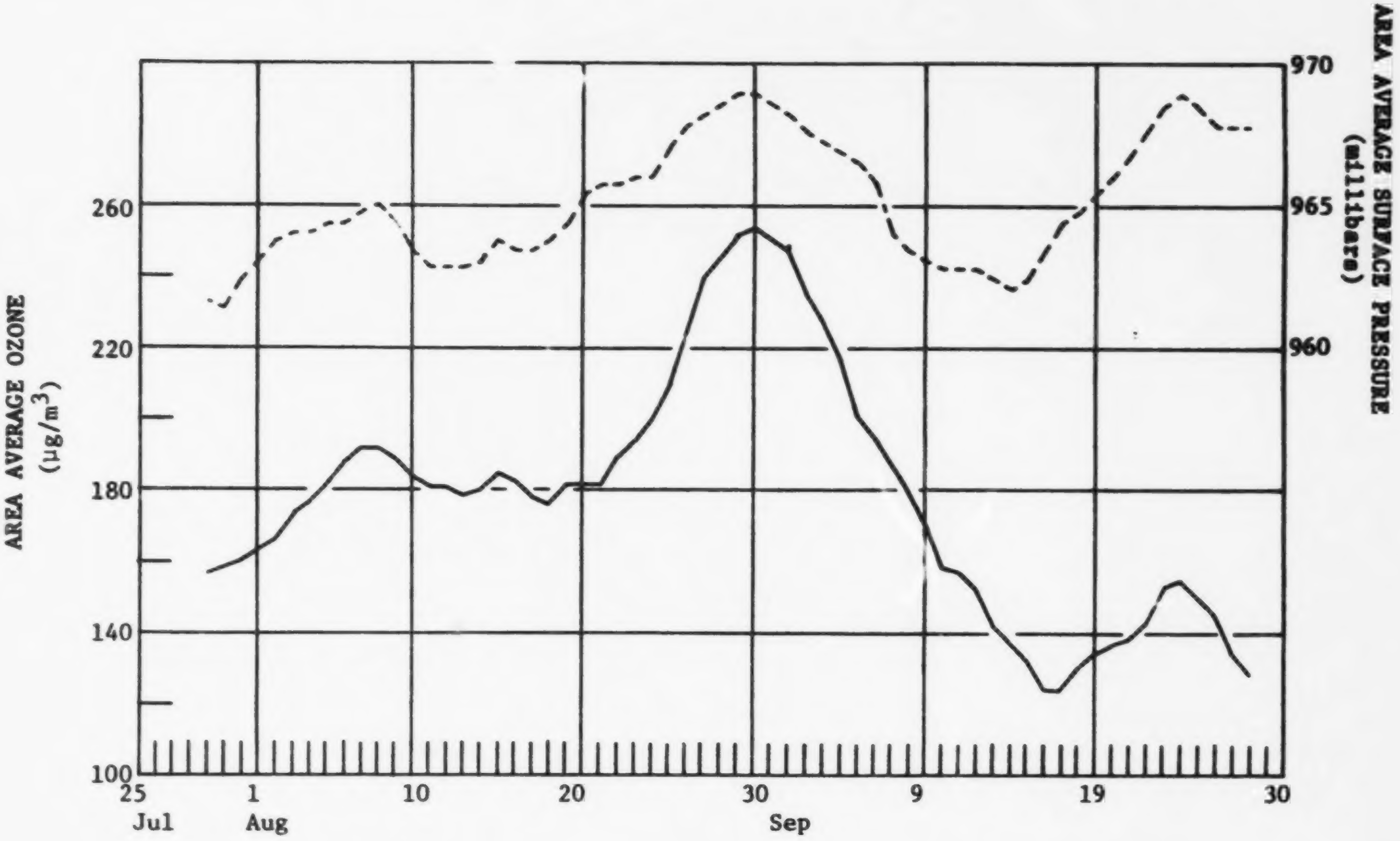


Figure 74. Nine-point running average of the data presented in figure 72.

these figures that periods of extermely high ozone are generally associated with periods of higher pressure, and low ozone with lower pressure. Generally, the lowest ozone concentration is found after the minimum pressure, which may be interpreted to mean that the lowest ozone concentrations occur after frontal passage when the leading edge of a high-pressure system is moving into the area. During time periods shown in the two figures, the area average maximum ozone concentration was greater than 160 $\mu g/m^3$, a greater percentage of the time than below that value.

6.3.3 Case Studies

The following represents a summary of three cases in which a high-pressure system moved into the area under study accompanied by a simultaneous increase in the concentration of ozone. Figure 75 presents the variation of average ozone concentration (average ozone concentration for the period 1200 EDT to 2000 EDT) for the period July 5-11, 1974. The stations represented are Wilmington, Ohio; McConnelsville, Ohio; Wooster, Ohio; DuBois, Pennsylvania; and McHenry, Maryland. The data indicate that after July 5, all stations experienced periods in which the ozone concentration exceeded 160 $\mu g/m^3$. The largest 8-hour average concentration, 282 $\mu g/m^3$, was found at McHenry on July 8.

On July 4, a high-pressure system was found to the northwest of the study area and was moving southeastward into the Ohio, Pennsylvania, Virginia, and West Virginia region. The center of the high-pressure system was found in the northeastern part of Ohio on July 6, approximately where the largest ozone concentration was reported (Wooster) (fig. 76a). The average ozone concentration exceeded 160 $\mu g/m^3$ at three of the stations. The surface winds on this date were small in magnitude (less than or equal to 3 m/s) over the area, and the surface flow was disorganized in the eastern portions of the United States (fig. 76b). During the daylight period, clouds obscured all stations where ozone was being measured, but Wooster had the minimum cloud cover of all these stations (fig. 76c). Skies were clear in south central Michigan, northeastern Indiana, and northwestern Ohio.

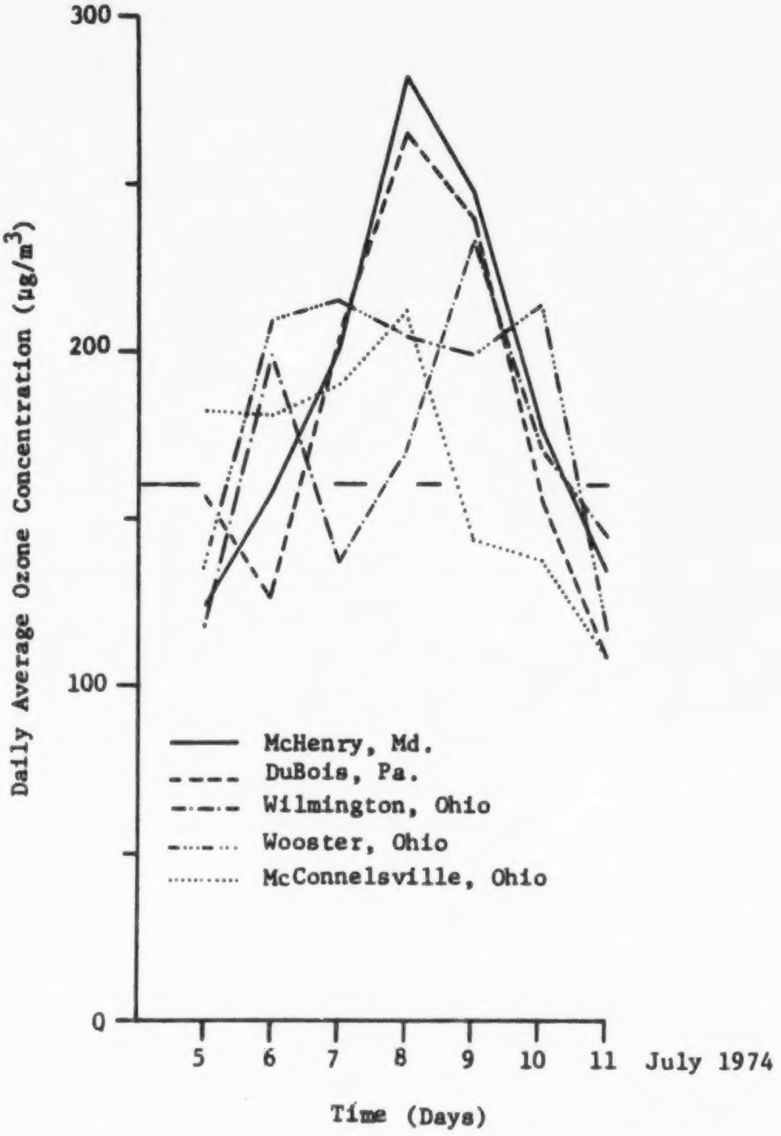
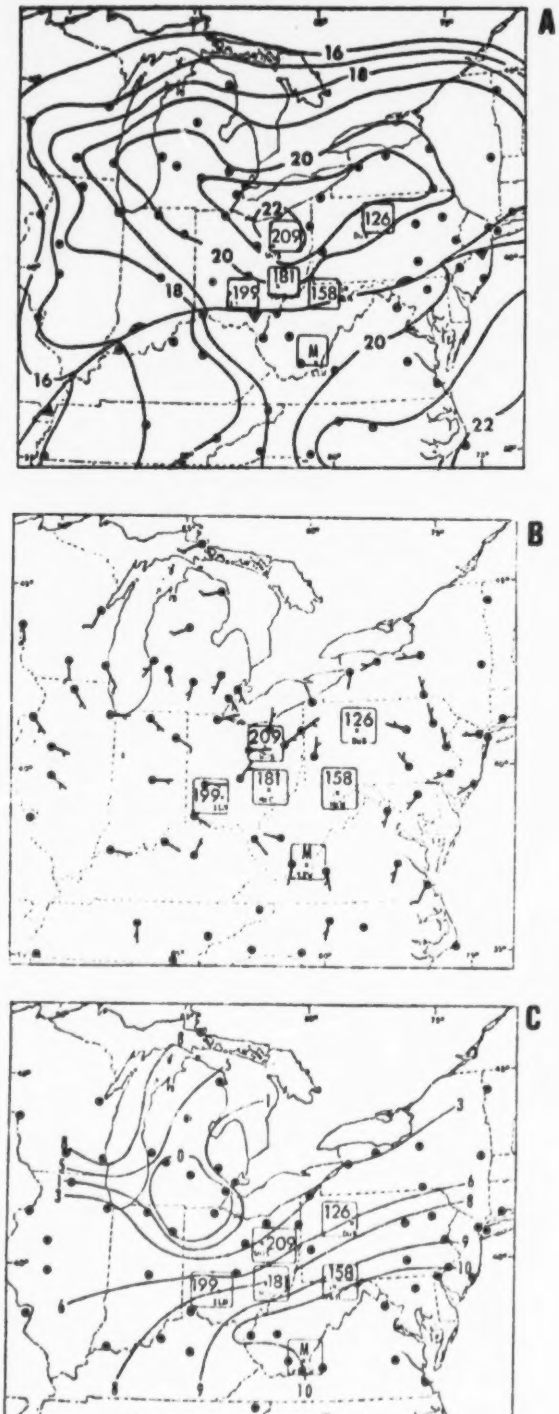


Figure 75. The variation of the 8-hour average value (1200 to 2000 EDT) of ozone (μg/m^3) for the period July 5-11, 1974, in the eastern United States.



A
16
18
20
22
209
126
181
199
158
M
20
18
16
20
22
B
126
209
181
158
199
M
C
3
0
6
8
9
10
126
209
199
181
158
M
10
6
8
9

Figure 76. a) Surface pressure (mb with only tens and units digits given) analysis (1700 EDT); b) resultant winds; c) mean cloud cover (tenths) (0700 to 1900 EDT) for July 6, 1974. Eight-hour average ozone values (μg/m^3) (1200-2000 EDT) indicated at each station.

The high-pressure system continued to drift slowly eastward, and on July 8, the center was in the western part of Pennsylvania (fig. 77a). The largest 8-hour average ozone concentration on that date was also found in this region; and all stations for which an average ozone concentration could be computed had concentrations larger than 160 $\mu g/m^3$. Again, the surface winds were generally weak over the area, and the surface flow was disorganized (fig. 77b). Clouds were evident at all ozone-reporting stations, and the amounts were 0.4 or less (fig. 77c).

The high-pressure system continued to move eastward as a front approached the region of interest. After the front passed all the stations in the area, the average concentration of ozone decreased markedly (fig. 78a). The average surface wind speed in the region was in excess of 10 mph, and an organized flow at the surface from the northeast characterized the region of interest (fig. 78b). All but one of the ozone stations (Wilmington) were in a region where the average daylight cloudiness was less than 0.4 (fig. 78c).

Figure 79 presents the average ozone variation (same 8-hour averages as before) for the period July 20-23, 1974, during which a high-pressure system moved into the area of interest. In this case, data from Wilmington, Ohio; DuBois, Pennsylvania; McHenry, Maryland; and McConnelsville and Wooster, Ohio were available. The data indicate a systematic increase of ozone at all stations, and the largest ozone concentrations were observed on July 22.

A high-pressure center was found to the north northwest of the region of interest on July 20. Unlike the previous case, the high center moved rapidly. On July 22, the highest 8-hour average ozone concentration was located at a station nearest to the center of high pressure, which was found off the northeast coast at 1700 EDT (fig. 80a). All stations but one had an 8-hour average ozone concentration exceeding 160 $\mu g/m^3$. The surface winds over the area on July 22 were generally weak (less than or equal to 3.0 m/s), but the surface flow was organized, having a direction from the southeast (fig. 80b). Clouds were found at each station reporting ozone concentrations with the station reporting the highest average ozone concentrations having the same amount of cloudiness as the station reporting the lowest average concentrations (= 0.7 cloud cover) (fig. 80c).

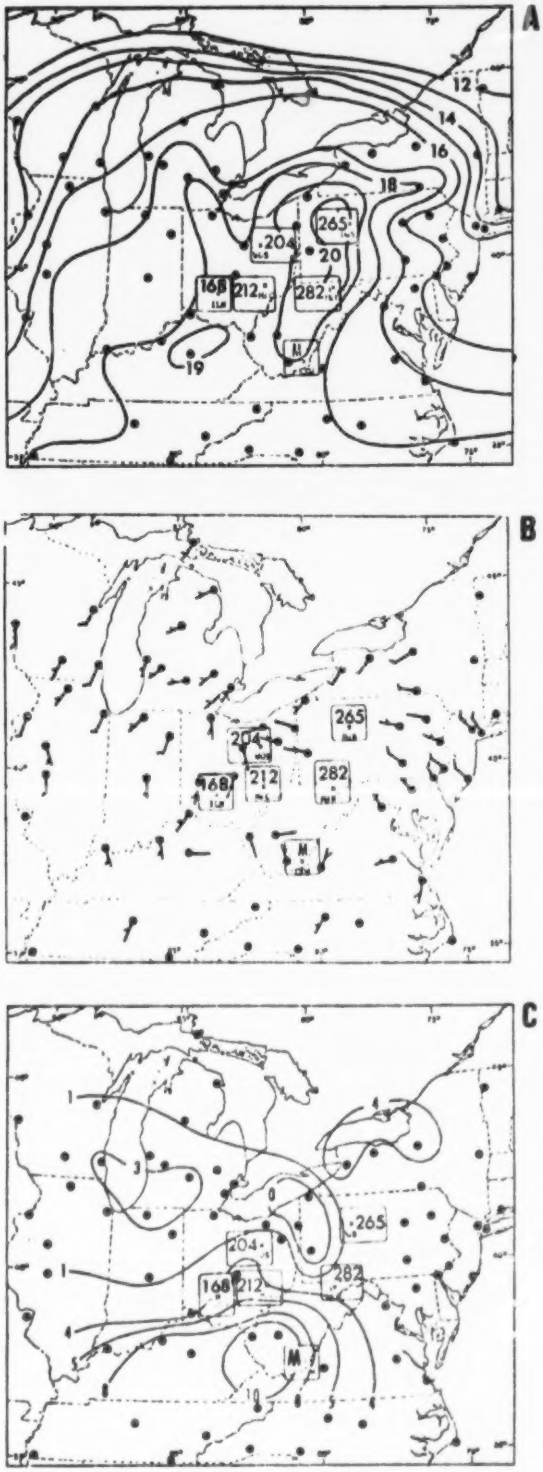

A
12
14
16
18
265
204
20
168
212
282
M
19
B
265
204
168
212
282
M
C
1
3
0
265
204
282
168
212
1
M
10
2

Figure 77. a) Surface pressure (mb with only tens and units digits given) analysis (1700 EDT); b) resultant winds; c) mean cloud cover (tenths) (0700 to 1900 EDT) for July 8, 1974. Eight-hour average ozone values ($\mu g/m^3$) (1200-2000 EDT) indicated at each station.

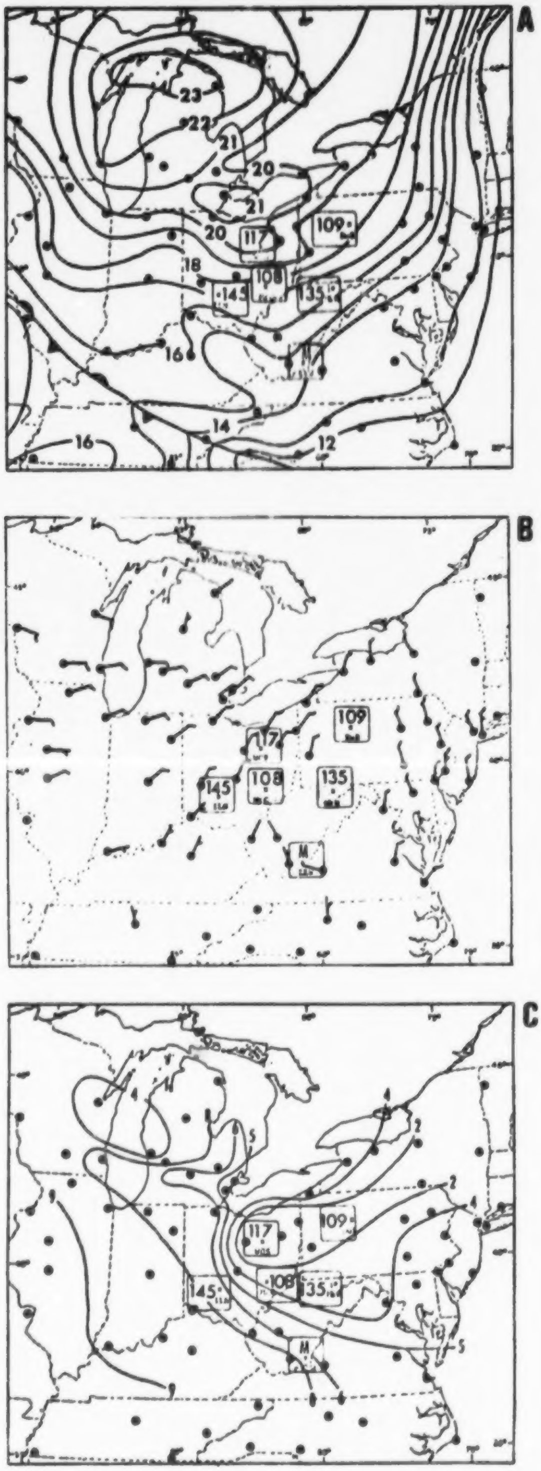

A
23
22
21
20
21
20
117
109
18
108
145
135
16
M
14
16
12
B
109
117
145
108
135
M
C
4
5
4
2
2
4
117
109
145
108
135
M
5

Figure 78. a) Surface pressure (mb with only tens and units digits given) analysis (1700 EDT); b) resultant winds; c) mean cloud cover (tenths) (0700 to 1900 EDT) for July 11, 1974. Eight-hour average ozone values (μg/m^3) (1200-2000 EDT) indicated at each station.

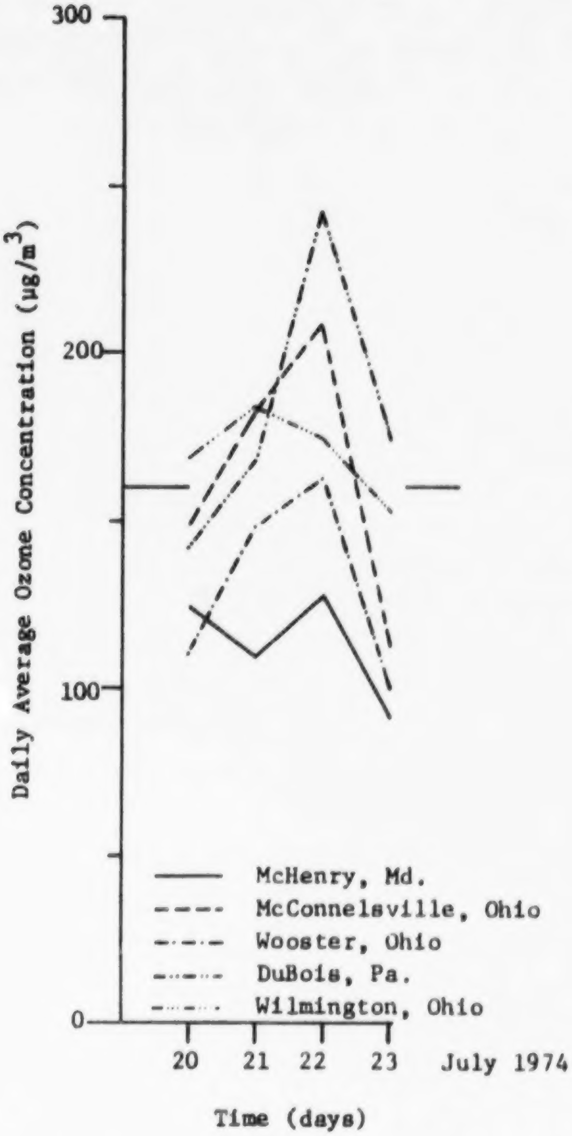


Figure 79. The variation of the 8-hour average value (1200 to 2000 EDT) of ozone (μg/m^3) for the period July 20-23, 1974, in the eastern United States.

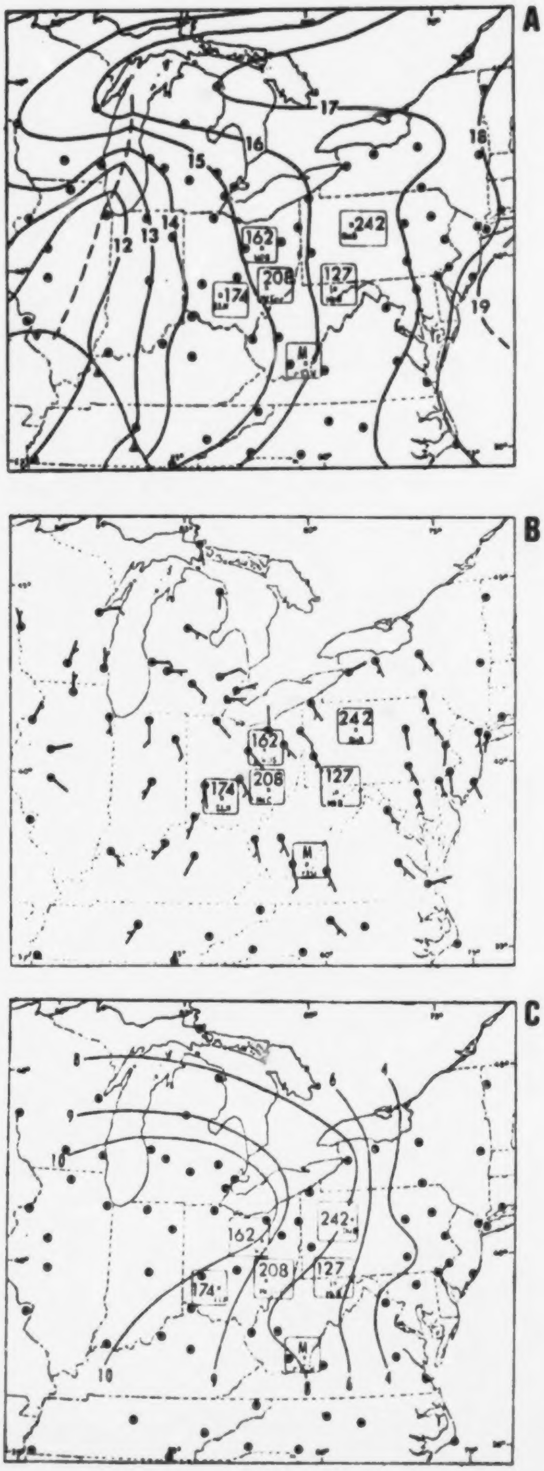

A
17
16
15
18
12
13
14
162
242
208
174
127
M
19
B
242
162
208
127
174
M
C
8
9
10
6
4
162
242
208
127
174
M
10

Figure 80. a) Surface pressure (mb with only tens and units digits given) analysis (1700 EDT); b) resultant winds; c) mean cloud cover (tenths) (0700 to 1900 EDT) for July 22, 1974. Eight-hour average ozone values ($\mu g/m^3$) (1200-2000 EDT) indicated at each station.

A cold front approached the region of interest on July 22 and was located through eastern Ohio on July 23. The average ozone concentration was lower at all stations on July 23 than on July 22 when cyclonic flow and overcast skies prevailed over the region of interest.

The highest concentrations of ozone encountered during the two summer periods in which ozone was observed occurred during the period August 25 to September 5, 1973. The 8-hour average ozone concentration (fig. 81) were greater than 160 $\mu g/m^3$ at all stations (McHenry, Maryland; Kane, Pennsylvania; Coshocton, Ohio; and Lewisburg, West Virginia) from the beginning to the end of the period. The largest single 1-hour average ozone concentration occurred at McHenry on August 28 and was 366 $\mu g/m^3$, which is almost equal to the 8-hour average ozone concentration on the same day and at the same station (350 $\mu g/m^3$).

During the period, a high-pressure system moved from the northeast. The center of the high was in West Virginia on August 26 and drifted into Kentucky on August 27 (fig. 82a). On August 27, the highest 8-hour average ozone concentration (350 $\mu g/m^3$) was found at Coshocton. Lewisburg, however, which was closer to the center of the high-pressure system, had the smallest concentration reported (193 $\mu g/m^3$), but it too exceeded 160 $\mu g/m^3$. The surface winds in Maryland, western, south central Pennsylvania, West Virginia, and southeastern Ohio were weak, and the surface flow was disorganized; whereas, north of that region, strong surface winds and organized flow from the southwest were found (fig. 82b). Kane had 0.8 cloud cover, but 0.1 to 0.2 cloud cover characterized the remainder of the stations observing ozone (fig. 82c).

The high-pressure center moved northward into Indiana and western Ohio on August 28, then moved eastward and was located in eastern Ohio and western Pennsylvania on August 29 (fig. 83a). McHenry had the highest 8-hour average value of ozone (307 $\mu g/m^3$), and Coshocton, the lowest (181 $\mu g/m^3$). Again, both maximum and minimum values exceeded 160 $\mu g/m^3$. The surface wind speeds were weak in the region of interest, and the surface flow was disorganized (fig. 83b). All stations had cloud cover. Kane and McHenry had the least cloud cover (≈ 0.2), and Coshocton had the most (≈ 0.6) (fig. 83c).

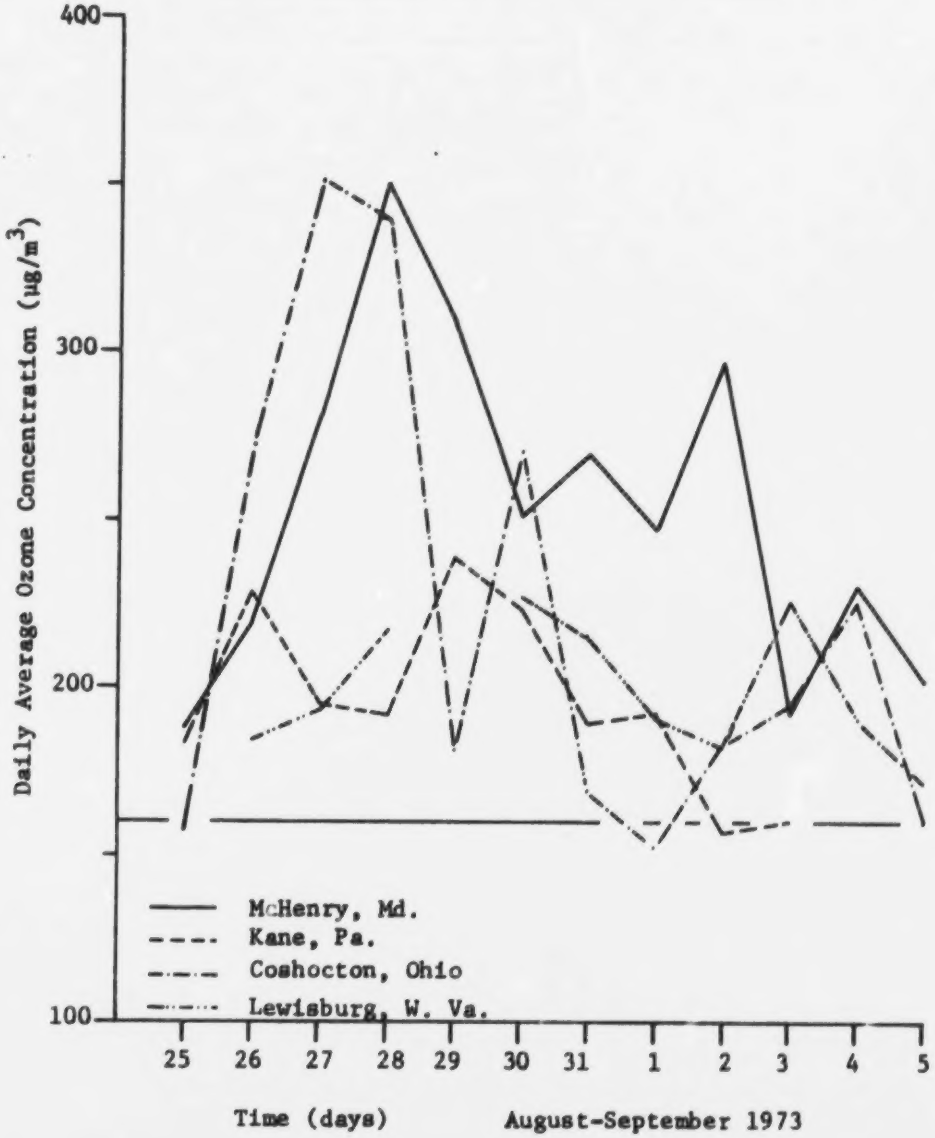


Figure 81. The variation of the 8-hour average value (1200 to 2000 EDT) of ozone (µg/m^3) for the period August 25 to September 5, 1973, in the eastern United States.

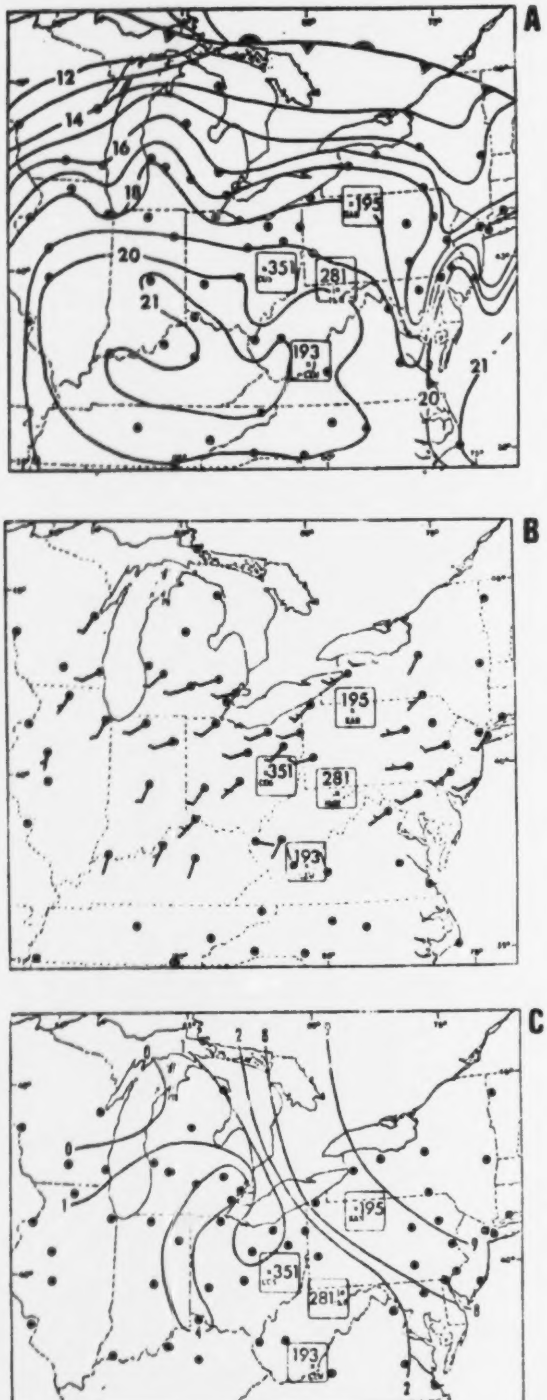
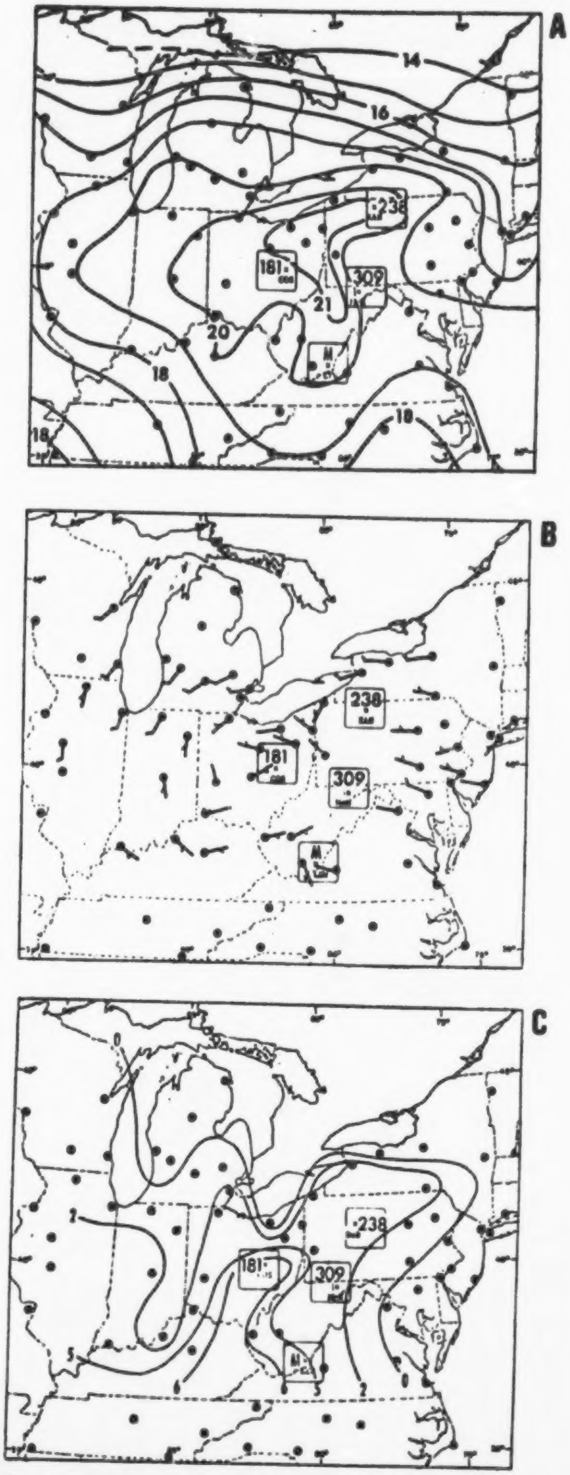

A
12
14
16
18
20
21
195
351
281
193
21
20
B
195
351
281
193
C
0
2
8
9
0
1
195
351
281
193
9
8
2

Figure 82. a) Surface pressure (mb with only tens and units digits given) analysis (1700 EDT); b) resultant winds; c) mean cloud cover (tenths) (0700 to 1900 EDT) for August 27, 1973. Eight-hour average ozone values (μg/m^3) (1200-2000 EDT) indicated at each station.



A
14
16
238
181
309
21
20
18
M
18
18
B
238
181
309
M
C
238
181
309
M
2
5
0
2
5
0

Figure 83. a) Surface pressure (mb with only tens and units digits given) analysis (1700 EDT); b) resultant winds; c) Mean cloud cover (tenths) (0700 to 1900 EDT) for August 29, 1973. Eight-hour average ozone values (μg/m^3) (1200-2000 EDT) indicated at each station.

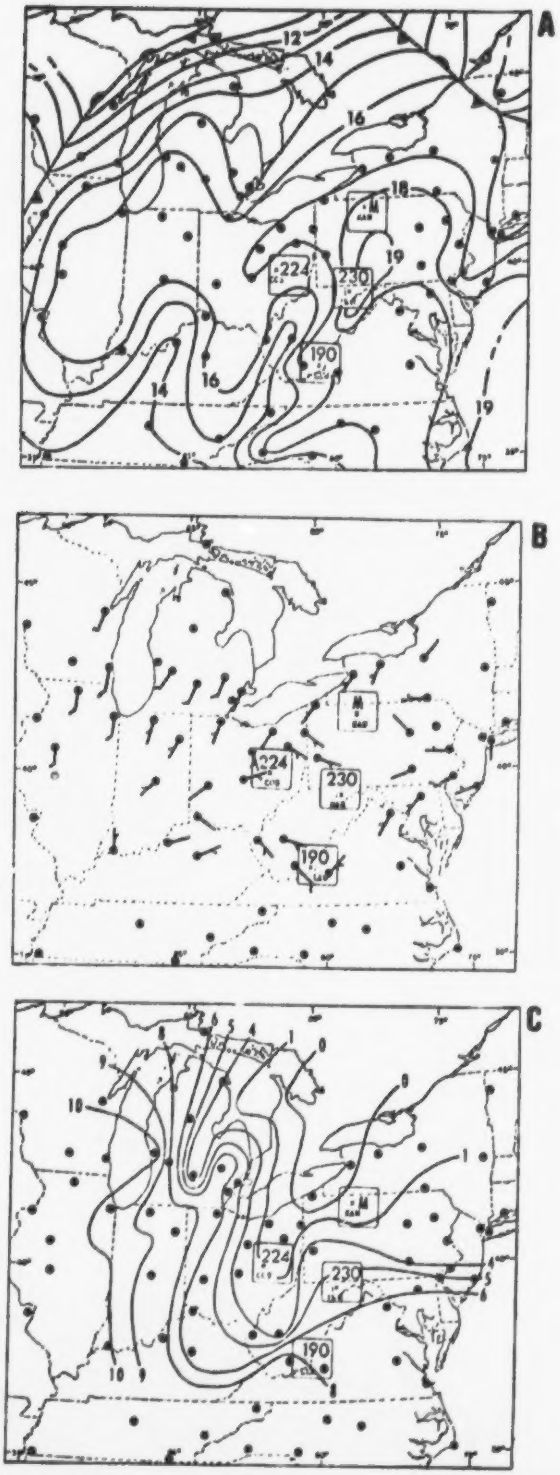
The center of high pressure continued to move eastward slowly and was found over McHenry on September 4 (fig. 84a). McHenry was also the station that experienced the highest value of the eight-hour average ozone concentration. Again, all reporting stations had eight-hour average values greater than 160 $\mu g/m^3$. The surface wind speeds were small over the area and the surface flow disorganized (fig. 84b). Less than 0.4 cloud cover was found over all stations with the exception of Lewisburg (fig. 84c). Lewisburg had more than 0.8 cloud cover, but yet had an eight-hour average ozone concentration of 190 $\mu g/m^3$ which was the lowest value reported on that day.

A rapid-moving cold front passed through the region of interest on September 5, and a new high-pressure center moved into the region from the northwest. The eight-hour average ozone concentrations were less than 160 $\mu g/m^3$ on September 6, but surpassed that value when the high-pressure center moved in from the northwest. It was not until a rather slow-moving low-pressure system began to move into the region on September 9 that the eight-hour average ozone concentrations remained below 160 $\mu g/m^3$ for more than 1 day.

6.3.4 Discussion of Meteorological Analysis

The preceding analysis is based on the data collected in the summers of 1973 and 1974 and may be subject to varied interpretation. The most plausible explanation resulting from this analysis is presented in the following discussion.

High pressure systems appear to provide appropriate environmental conditions for the production of high concentrations of ozone (greater than the NAAQS) over large areas (at least the order of 1.8 x 10^5 square kilometers). The highest ozone concentrations were found at observing stations near centers of the high pressure. These central areas were characterized by weak winds, disorganized flow, and relatively clear skies. Some cloud cover was present in each of the cases studied, but complete overcast conditions did



A
12
14
16
18
19
224
230
M
190
14
16
19
B
M
224
230
190
C
10
9
8
6
5
4
1
0
0
1
M
224
230
190
10
9
8
4
5
6

Figure 84. a) Surface pressure (mb with only tens and units digits given) analysis (1700 EDT); b) resultant winds; c) mean cloud cover (tenths) (0700 to 1900 EDT) for September 4, 1973. Eight-hour average ozone values (μg/m^3) (1200-2000 EDT) indicated at each station.

not occur when there were high ozone concentrations. Furthermore, it appears that the amount of cloudiness, other than complete overcast, does not have a marked influence on the production of ozone. To some degree, the maximum ozone concentration appears to be affected by the length of time high pressure center remains in a particular region; the longer the high pressure center persists, the higher the concentrations of ozone.

The lowest ozone concentrations were found after frontal passages. The eight-hour average ozone concentration for the 1200 to 2000 EDT period fell below 160 $\mu g/m^3$ only after the passage of a frontal system and its associated trough of low pressure. While the ozone concentration reached a minimum, following the passage of the trough, it did not always fall below the NAAQS.

As discussed earlier, mechanisms that can increase ozone concentrations in the surface layer are synthesis--given the required precursors and solar radiation--and vertical mixing--under conditions such that the ozone concentration increases with height in the mixing layer. In the weak, disorganized flow and clear skies associated with the central areas of high pressure system conditions are appropriate for the development of strong, surface-based, radiation induced, nocturnal thermal inversions. In such inversion layers gas phase reactions and contact with vegetation and other objects on the earth's surface cause ozone destruction. By morning the ozone concentration near ground level is considerably lower than existed during the preceding evening hours, and the concentration increases with height. After sunrise heating of the earth's surface takes place and the radiation inversion is replaced by a thermally unstable layer. Within this unstable layer, convective circulation will mix the higher concentrations of ozone from aloft with the lower concentrations near the surface, effectively increasing the near-surface concentration of ozone relative to the minimum value that occurred near sunrise. This process is illustrated by the ozone concentration profiles shown in figure 58. On the particular day illustrated, mixing could have accounted for approximately 50 percent of the increase of ozone concentration near the surface from early morning until late afternoon. An increase of ozone concentration from this process alone cannot produce concentrations at the surface as high as was experienced during the preceding day because some of the ozone in the mixed layer was destroyed during the intervening night. Day-to-day increases in ozone concentration can be accounted for only by synthesis.

There is no doubt that photochemical reactions can produce ozone in high concentrations in the relatively cloud-free regions of high pressure systems if there are appropriate concentrations of ozone precursors. The required precursors for ozone synthesis may be of natural or anthropogenic origin. Sources of both types of precursors are abundant in the region of the study; natural precursors from the vegetation and anthropogenic precursors from urban, industrial, and vehicular activities (figure 85). The distribution of these precursors in a high pressure system could be expected to be relatively uniform after a period of a few days except in the vicinity of well defined source areas such as urban-industrial centers. Since precursors of ozone are also destructive agents, injections from such well defined source areas initially may cause reductions in ozone concentrations, producing inhomogenieties in the overall ozone concentration. In the central region of a high pressure system the lack of organized wind flow produces thorough mixing, and abundant solar radiation makes conditions ideal for the production of high ozone concentrations. These conditions are repeated on a day-to-day basis so the central region of the high pressure system (the region of highest pressure) will usually have the highest concentrations of ozone. This process does not require the transport of the center of highest ozone concentration per se. The characteristics of the air mass

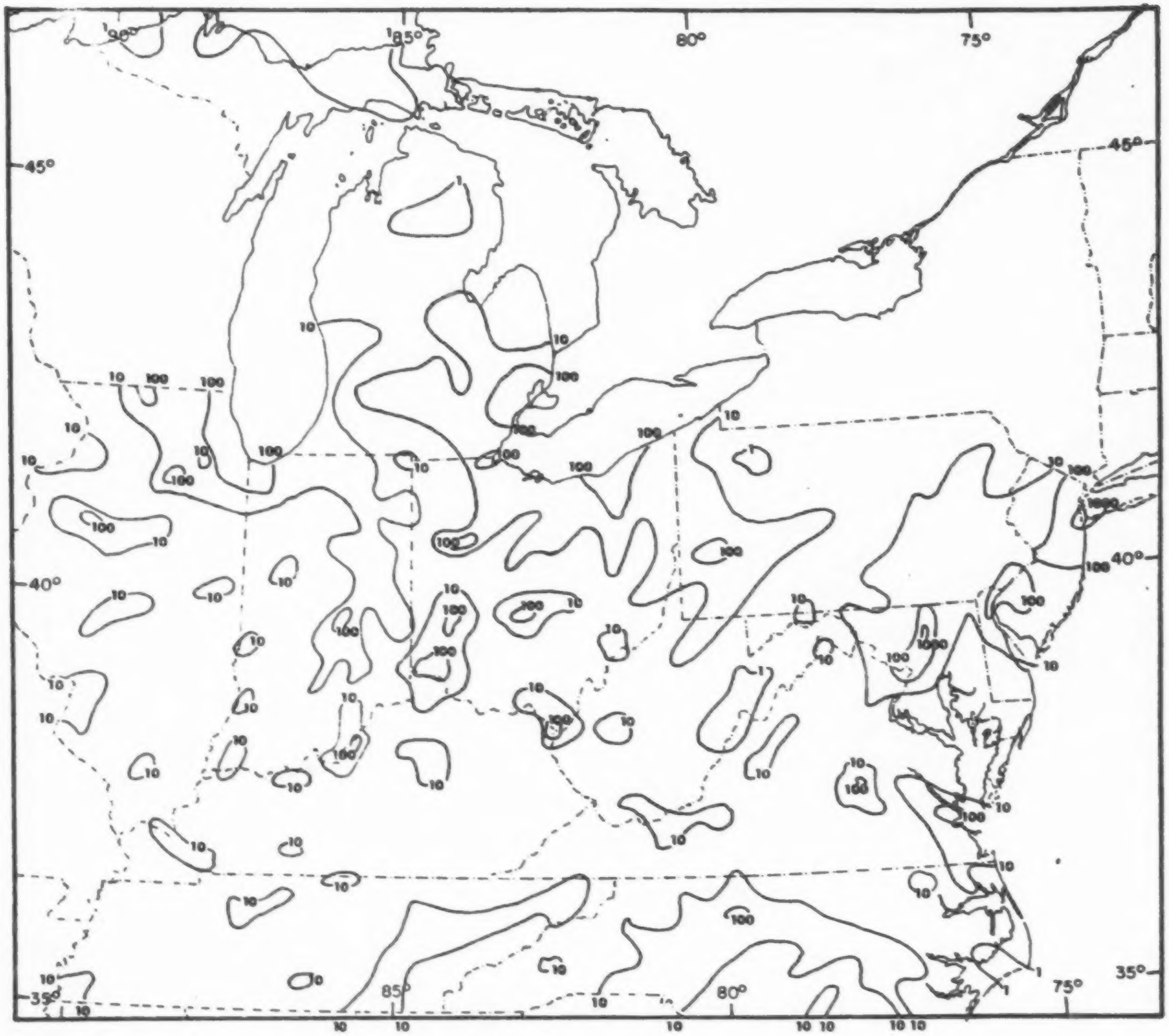

90°
85°
80°
75°
45°
40°
35°
10
100
1000
1

Figure 85. Average annual hydrocarbon emissions density, 1970 tons mi^{-2}.
Source: National Emissions Data Summary.

association with the unique conditions in the center of the high pressure system will produce, on a daily basis, the highest ozone concentrations.

At present, data are inadequate to permit postulation of the relative contributions of anthropogenic and natural precursors to the high concentrations measured in high pressure systems over the study area. Estimation of the relative contributions may be possible if a high pressure system can be studied from its source region into an area of higher emission rates of anthropogenic precursors.

6.4 Air Trajectories

Trajectories were numerically computed for air parcels arriving over the Garrett County, DuBois, McConnelsville, and Wilmington locations at 900 m (3000 ft MSL) at each 0000 and 1200 GMT from June 16 to September 1, 1974. Winds at 900 m (3000 ft) were extracted from the teletype data transmissions for the 16 rawinsonde stations within and surrounding the study area and were used as the basic input data for the numerical computations.

Trajectories were computed for the forty eight-hour period prior to the air mass's arrival in two-hour increments, based on spatially weighted (inverse distance) horizontal displacements, linearly interpolated in time. The plotted trajectories for each day are given in appendix F.

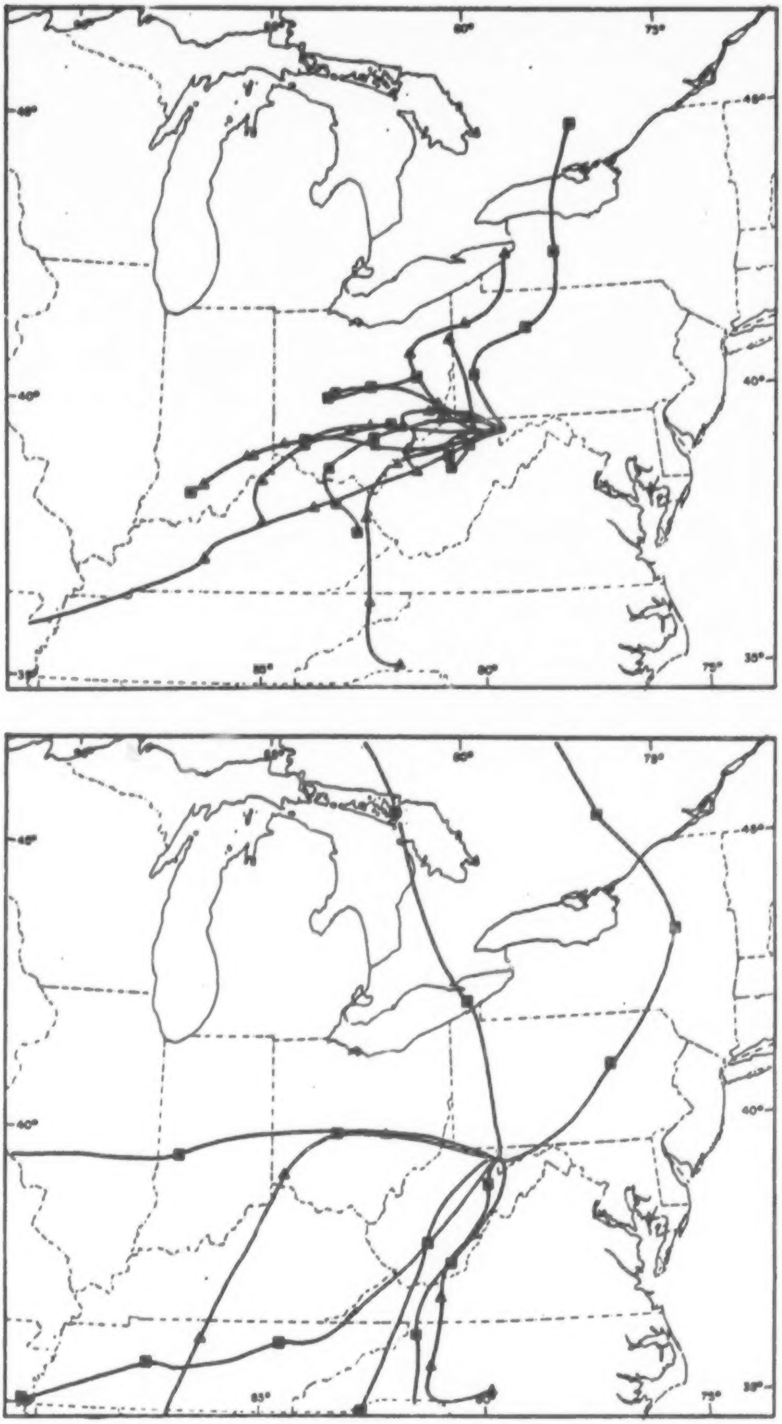
Twelve-hour average ozone concentrations were computed for each of the five ozone monitoring locations for the period six hours before to six hours after 0000 GMT or 1200 GMT (1400 to 0200 EDT and 0200 to 1400 EDT). The central times are the same as the trajectory arrival times. The dates and times of the high ozone concentrations--when the twelve-hour average ozone concentration exceeded the upper decile concentration--were noted for Garrett County, McConnelsville, and DuBois. Trajectories for air arriving at each station associated with high ozone were plotted. Similarly low ozone--for data in the lowest decile concentrations--trajectories were plotted for each of the three stations. The trajectories for high and low ozone concentrations are shown in figures 86a, 86b, and 86c.

The ozone trajectories at Garrett County arrive from the west southwest through northeast at a slow speed, especially during the last twelve hours of the trajectory. Although most trajectories cross east central Ohio and northern West Virginia during that time, the earlier positions (24 to 48 hours before arrival) of the trajectories do not suggest a preferred source region for high ozone at Garrett County. Low ozone concentrations, although infrequent, are obviously associated with rather rapidly-moving air. No directional preference for low ozone trajectories is apparent.

Previous studies have shown upper decile ozone concentrations at Garrett County are associated with trajectories crossing the lower Michigan, northern Ohio area, or moving northeastward parallel to the ridgelines of the Appalachian Mountains of West Virginia, but not from east central Ohio as shown in 1974. Part of the reason for the difference may lie in preferred wind directions of the seasons resulting from different pressure patterns and pressure system movements.

At DuBois, the high ozone concentration is associated with air moving primarily from the west across Ohio, which arrives during the day or night. Wind speeds are generally higher than those noted at Garrett County. At other times the trajectories crossing much of the same areas, including the Ohio River Valley and the southern side of the Great Lakes, are associated with low ozone concentrations, probably because they move faster. These trajectories show no particular preference of arrival time.

In speed, direction, and area coverage, the high ozone trajectories arriving at DuBois are quite like those which arrived at Kane, Pennsylvania, during the 1973 study. The low ozone trajectories which arrived at Kane had a much more northwesterly origin, but moved at speeds comparable to low ozone trajectories arriving at DuBois.

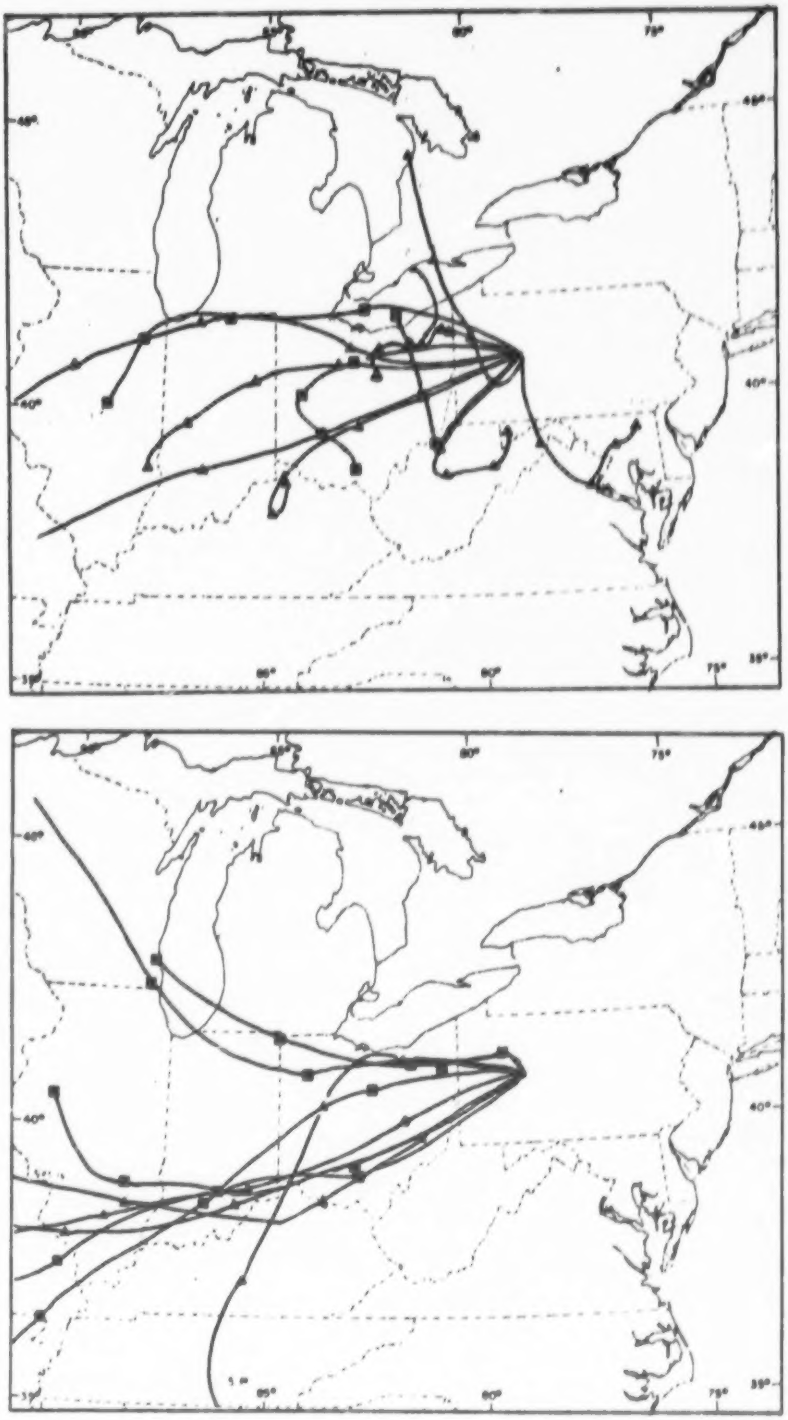


$O_3 \geq 168$ µg/m^3

Garrett County

$O_3 < 62$ µg/m^3

Figure 86a. Air parcel trajectories arriving at three locations for the indicated 12-hour average ozone concentrations. The triangles (Δ) indicate the 12, 24, 36 and 48-hour positions of parcels arriving at 0000 GMT; the squares (▢) represent those parcels arriving at 1200 GMT.

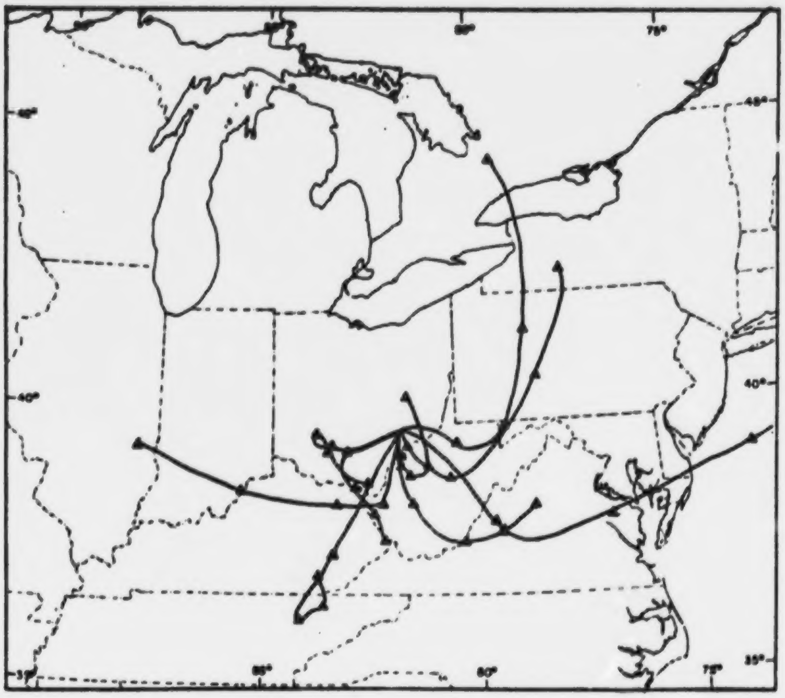


$O_3 \geq 200\ \mu g/m^3$

DuBois

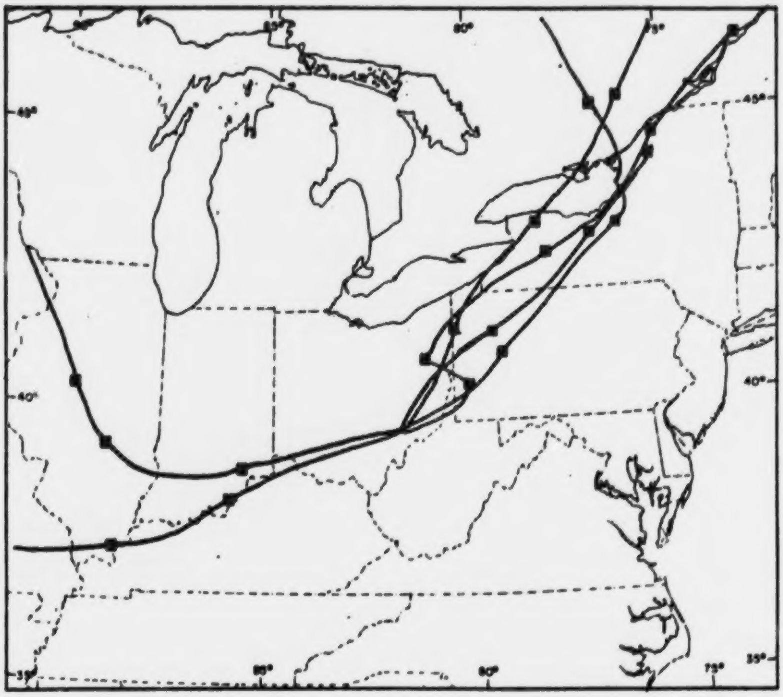
$O_3 < 48\ \mu g/m^3$

Figure 86b. Air parcel trajectories arriving at three locations for the indicated 12-hour average ozone concentrations. The triangles (Δ) indicate the 21, 24, 36 and 48-hour positions of parcels arriving at 0000 GMT; the squares (□) represent those parcels arriving at 1200 GMT.



$O_3 > 168\ \mu g/m^3$

McConnelsville



$O_3 < 45\ \mu g/m^3$

Figure 86c. Air parcel trajectories arriving at three locations for the indicated 12-hour average ozone concentrations. The triangles (Δ) indicate the 12, 24, 36 and 48-hour positions of parcels arriving at 0000 GMT; the squares (□) represent those parcels arriving at 1200 GMT.

The trajectories associated with high ozone concentrations at the McConnelsville site show a unique arrival pattern: all arrive from locations east through south to west-southwest of the site. The trajectories have origins (48-hour positions) in the north through east and into the west, but none come from the northwest, across central Ohio. Although some high ozone trajectories indicate rapid movement, the last 12-hour movements are slower. All of these trajectories arrive at 0000 GMT. That the low ozone trajectories arrived at 1200 GMT is a reflection of the strong diurnal range of ozone at McConnelsville. As in other cases, the speeds are greater, yet the air appears to have moved along the Ohio River Valley or from the northeast. Neither path is free of industrial or population centers.

The high and low ozone trajectories computed for McConnelsville in 1974 bear no resemblance to similar trajectories computed in 1973 for Coshocton, Ohio, which is 72 km (45 mi.) to the north.

The strong diurnal character of high or low ozone at McConnelsville as well as the diurnal average of ozone (fig. 31) suggest that nocturnal radiative inversions effectively limit the vertical mixing of ozone and its destructive agents, thus allowing the destruction of ozone near the ground.

That the high and low ozone trajectories arriving at DuBois oftentimes follow the same course suggests that the path taken by the air does not have a substantial impact upon the ozone concentrations. The year-to-year variability of the areas associated with high or low ozone concentration further supports this idea.

The speed of movement of the air, especially in the 12 hours prior to arrival, did seem inversely related to the ozone concentration. If the recent movement was slow, conditions are stagnant; the ozone concentration was higher than in other cases where recent air movement was faster.

6.5 Chemistry of Ozone Generation

The evidence indicates that high ozone concentrations observed in rural areas probably did not just originate in the cities and drift, unaffected, downstream. The most telling argument for this is that the maximum ozone and average concentrations measured in the large cities of the study area were lower than those measured at the rural sampling sites. If drift of urban ozone alone were responsible for the high rural concentrations, urban concentrations would be equal to or higher than rural concentrations. Therefore, some of the ozone measured at the rural sites was generated as the air moved from the cities to and beyond the sampling sites.

Data taken before the mid-1960's indicate no such elevated concentrations of ozone in rural areas as have been observed in this study. Reference is here made to the ozone section of Junge's "Air Chemistry and Radioactivity";[1/] also see table 34, reproduced from Junge, which summarizes data from a number of observers. Regener's study at O'Neil, Nebraska, in the summer of 1953 is particularly pertinent (average ozone, 60 $\mu g/m^3$, range 30-100 $\mu g/m^3$). RTI-UNC investigations from 1964 to 1967 in the mountains, and piedmont of North Carolina and at sea did not encounter the high non-urban phenomenon as it existed in the Ohio Valley in the summer of 1974. The point of these results (Regener, Junge and RTI-UNC) with regard to the high non-urban O_3 concentrations is that no high (≥ 160 $\mu g/m^{-3}$) concentrations were observed previously in a number of kinds of natural environments. Earlier investigators did not observe the high concentrations of ozone now being measured. The argument that this increase in rural ozone is an artifact of change in instrumentation (KI to chemiluminescent) cannot be supported, because compounds known to interfere with the KI method (i.e., SO_2 and H_2S) do not occur in sufficient concentrations in most of the truly remote areas. The data presented in figure 58 are the best argument for the occurance of O_3 synthesis in the atmosphere's boundary layer.

It is improbable that any different types of reactions are occurring to cause generation of the ozone at rural sites that do not also occur in the urban air. Natural precursors should also enter into these reactions. The major difference between hypothetically natural air and the urban-rural mixture lies in its past history. At one time part of the mixture possessed higher concentrations of ozone precursors than those which were measured at the rural site. The possible importance of this is that the urban portion of the mixture would have contributed greater concentrations of stable intermediates which are capable of generating hydroxyl and hydroperoxyl radicals.

Table 34. Concentrations of tropospheric ozone as given in more recent and extensive studies (From Junge, "Air Chemistry and Radioactivity".1/)

Observer	Location, time, and remarks	Altitude	O_3 ($\mu g/m^3$)	
			Range[a]	Average
Götz and Volz (1951)	Arosa, Switzerland, 1950-51, high valley, daily maxima values	1860 meters	19-90	50
Regener (1957)	Mt. Capillo, and Albuquerque, New Mexico, 1951-52	3100 meters	18-85	45
		1600 meters	3-120	36
Regener (1957)	O'Neil, Nebraska, 1953	12.5 meters above ground	30-100	60
Ehmert (1952)	Weissenau, Bodensee, Germany, 1952	20 meters above ground	0-90	35
			0-70	30
Teichert (1955)	Lindenberg Obs., Germany, 1953-54	80 meters above ground	0-50	30
			0-50	27
Kay (1953)	Farnborough, England, 1952-53	0-12,000 meters	26-50	38
Brewer (1955)	Tromsö, Norway, 1954	0-10,000 meters	60-70	65
Price and Pales (1959)	Mauna Loa Observatory, Hawaii	3000 meters	30-62	45
Wexler et al. (1960)	Little America Station, Antarctica	100 meters	20-60	45

[a] As interpreted from the published data. The values sometimes represent absolute maxima, sometimes mean maxima.

Table 35. Summary of simulated time-concentration profiles for propylene-NO_x chemistry[a,b]/

Time (Min)	[HC]	$[NO_2]$	[NO]	$[CH_2O]$	[RCHO]	$[O_3]$
0	0.33	0.10	0	0	0	0
65	0.23	0.83×10^{-1}	0.88×10^{-2}	0.84×10^{-1}	0.78×10^{-1}	0.14
125	0.15	0.76×10^{-1}	0.51×10^{-2}	0.13	0.12	0.22
184	0.88×10^{-1}	0.65×10^{-1}	0.36×10^{-2}	0.14	0.14	0.28
245	0.52×10^{-1}	0.56×10^{-1}	0.27×10^{-2}	0.13	0.14	0.31
305	0.31×10^{-1}	0.48×10^{-1}	0.22×10^{-2}	0.11	0.13	0.33
365	0.18×10^{-1}	0.41×10^{-1}	0.18×10^{-2}	0.93×10^{-1}	0.12	0.35
425	0.10×10^{-1}	0.35×10^{-1}	0.15×10^{-2}	0.76×10^{-1}	0.10	0.36
485	0.59×10^{-2}	0.31×10^{-1}	0.13×10^{-2}	0.61×10^{-1}	0.92×10^{-1}	0.36
545	0.34×10^{-2}	0.26×10^{-1}	0.11×10^{-2}	0.49×10^{-1}	0.81×10^{-1}	0.37
604	0.19×10^{-2}	0.23×10^{-1}	0.95×10^{-3}	0.40×10^{-1}	0.70×10^{-1}	0.38

[a] Initial Conditions: $[HC]_o$ (Propylene) $\tilde{=}$ 1 ppmc (0.33 ppmv); $[NO_2]_o \sim 0.10$; $\Phi ka = 0.4$ minutes^{-1}

[b] Concentration units: ppmv

Table 36. Summary of simulated time-concentration profiles for propylene-NO_x chemistry[a,b]/

Time (Min)	[HC]	$[NO_2]$	[NO]	$[CH_2O]$	[RCHO]	$[O_3]$
0	0.67	0.20	0	0	0	0
66	0.37	0.16	0.72×10^{-2}	0.24	0.21	0.31
123	0.18	0.12	0.40×10^{-2}	0.31	0.28	0.43
183	0.87×10^{-1}	0.86×10^{-1}	0.26×10^{-2}	0.29	0.28	0.48
243	0.42×10^{-1}	0.64×10^{-1}	0.19×10^{-2}	0.24	0.26	0.50
303	0.20×10^{-1}	0.49×10^{-1}	0.14×10^{-2}	0.19	0.24	0.52
363	0.10×10^{-1}	0.37×10^{-1}	0.10×10^{-2}	0.15	0.21	0.52
423	0.49×10^{-2}	0.28×10^{-1}	0.77×10^{-3}	0.12	0.19	0.53
483	0.24×10^{-2}	0.20×10^{-1}	0.54×10^{-3}	0.91×10^{-1}	0.16	0.54
543	0.11×10^{-2}	0.13×10^{-1}	0.34×10^{-3}	0.71×10^{-1}	0.14	0.54
603	0.52×10^{-3}	0.68×10^{-2}	0.17×10^{-3}	0.56×10^{-1}	0.12	0.54

[a] Initial Conditions: $[HC]_o$ (Propylene) $\cong$ 2 ppmc (0.67 ppmv); $[NO_2]_o \sim 0.1$ ppm; $\Phi ka = 0.4$ minutes^{-1}

[b] Concentration units: ppmv

Kopczynski et al[15] found that dilution of his initial reactants (in this case, aldehydes and NO_x) reduced the net ozone concentrations obtained by a lesser percentage than the initial reactants. Reasoning by analogy one can postulate that the chemical intermediate behave similarly. Computer simulations shown in tables 35 and 36 suggest also that dilution of the ozone precursors is accompanied by a smaller net percentage decrease in concentrations of ozone and or some of the secondary pollutants such as aldehydes. These computer simulations are based on the set of reaction mechanisms compiled by Jeffries and Sickles[16] (see table 37). Computer simulation suggests also that the stable intermediates left from a previous run with simulated urban concentration plus low concentrations of hydrocarbon and NO_2 can generate greater concentrations of ozone than the sum of each system ran separately.

Although there are many pathways of •OH generation the photolysis of aldehydes offers one of the most productive in terms of each molecule's involvement.

Hydroxyl Radical Formation

1. $CH_2O + h\nu \longrightarrow H\cdot + H\dot{C}O$

   $H + O_2 \longrightarrow HOO\cdot$

   $H\dot{C}O + O_2 \longrightarrow CO + HOO\cdot$

   $HOO\cdot + NO \longrightarrow NO_2 + \cdot OH$

2. $RCHO + h\nu \longrightarrow R\cdot + H\dot{C}O$

   $R + O_2 \longrightarrow RO_2$

   $RO_2 + NO \longrightarrow NO_2 + RO\cdot$

   $H\dot{C}O + O_2 \longrightarrow CO + HOO\cdot$

   $HOO\cdot + NO \longrightarrow NO_2 + \cdot OH$

Further Peroxy Radical Formation

$RH + \cdot OH \longrightarrow R\cdot + H_2O$

$R\cdot + O_2 \longrightarrow ROO\cdot$

Table 37. Jeffries'-Sickles' reaction mechanism[a]

Reaction	Reaction Rate Constant
$h\nu + NO_2 = NO + O$	0.40
$h\nu + HNO_2 = OH + NO$	0.133
$h\nu + H_2O_2 = 2\ OH$	2.2 E-4*
$h\nu + CH_2O = CO$	4.4 E-3
$h\nu + CH_2O = HO_2 + CO$	8.0 E-4
$h\nu + RCHO = ROO + HO_2$	3.5 E-4
$h\nu + RCHO = CO$	1.75 E-5
$h\nu + O = O_3$	4.16 E 6
$NO + O_3 = NO_2$	2.4 E 1
$O + NO_2 = NO$	1.34 E 4
$O_3 + NO_2 = NO_3$	4.59 E-2
$NO_3 + NO = NO_2$	1.28 E 4
$NO_3 + NO_2 = N_2O_5$	5.58 E 3
$N_2O_5 = NO_2 + NO_3$	1.55 E 1
$N_2O_5 = 2\ HNO_3$	5.0 E-6
$NO_2 + NO = 2\ HNO_2$	3.2 E-5
$OH + NO_2 = HNO_3$	6.5 E 3
$OH + NO = HNO_2$	1.2 E 4
$OH + CO = HO_2$	2.5 E 2
$OH + H_2O_2 = HO_2$	1.2 E 3
$OH + HO_2 =$	1.2 E 4
$HO_2 + NO = OH + NO_2$	2.0 E 2
$HO_2 + O_3 = OH$	4.5 E 0
$HO_2 + HO_2 = H_2O_2$	5.3 E 3
$OH + CH_2O = HO_2 + CO$	2.1 E 4
$HO_2 + CH_2O = H_2O_2 + CO + HO_2$	2.1 E-2
$OH + RCHO = RCO_3$	2.2 E 4
$HO_2 + RCHO = RCO_3 + H_2O_2$	1.1 E-2
$O + C_3H_6 = R'OO + HO_2 + CO$	5.3 E 3
$HO_2 + C_3H_6 = RHO_4 + RCHO$	1.1 E 0
$OH + C_3H_6 = R'OO + CH_2O$	1.25 E 4

---

[a] This mechanism is continuously being revised and refined.

*E - Exponential

Ozone Formation

$$NO_2 + h\nu \longrightarrow NO + O$$

$$O + O_2 \xrightarrow{M} O_3$$

$$O_3 + NO \longrightarrow NO_2 + O_2$$

$$ROO\cdot + NO \longrightarrow NO_2 + RO\cdot \text{ (one } O_3 \text{ preserved)}$$

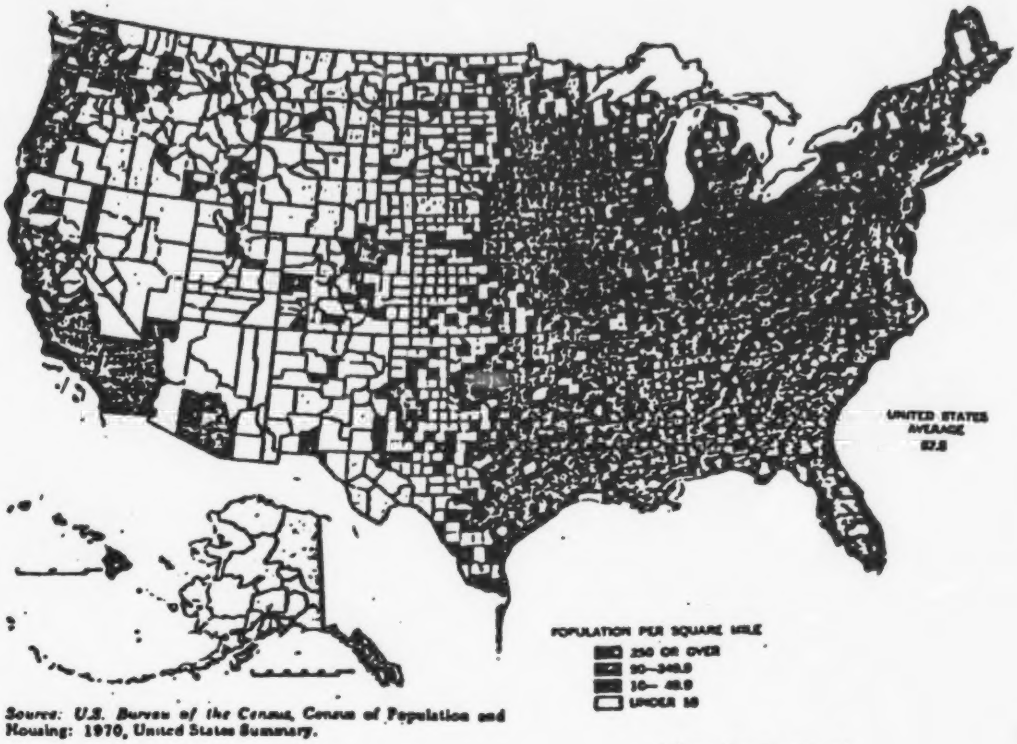
Although other processes may enter into the generation of the ozone concentrations observed at the rural sampling sites, the process postulated here must account for a considerable portion.

The hypothesis is that the high ozone concentrations observed in the rural areas are formed by the same reactions which generate ozone in the city. In the rural areas where measurements have been made, the ozone precursors, hydrocarbons and oxides of nitrogen, are most likely a mixture of material from anthropogenic-urban, anthropogenic-rural, and natural sources. The ozone is formed in transit to or in situ at the rural sampling sites. One contribution of the city air is to provide a slightly higher concentration ot ozone precursors, but the major contribution of the urban air is to provide the stable intermediate which will provide enough ·OH radicals upon solar irradiation to drive the NO + ROO· reaction at a rate in the neighborhood of 1.5 pphm hr^{-1} or greater.

6.6 Postulated Sequence for Ozone Generation and Destruction in Rural Areas

Figure 87 is a population map of the United States, and figure 88 shows the typical movement of typical northern United States' high-pressure centers which travel from sparsely populated areas into the more densely populated areas and on out to sea. (These samples are for August 1973.) A relationship between high-pressure and high ozone concentration has been shown in section 6.3.

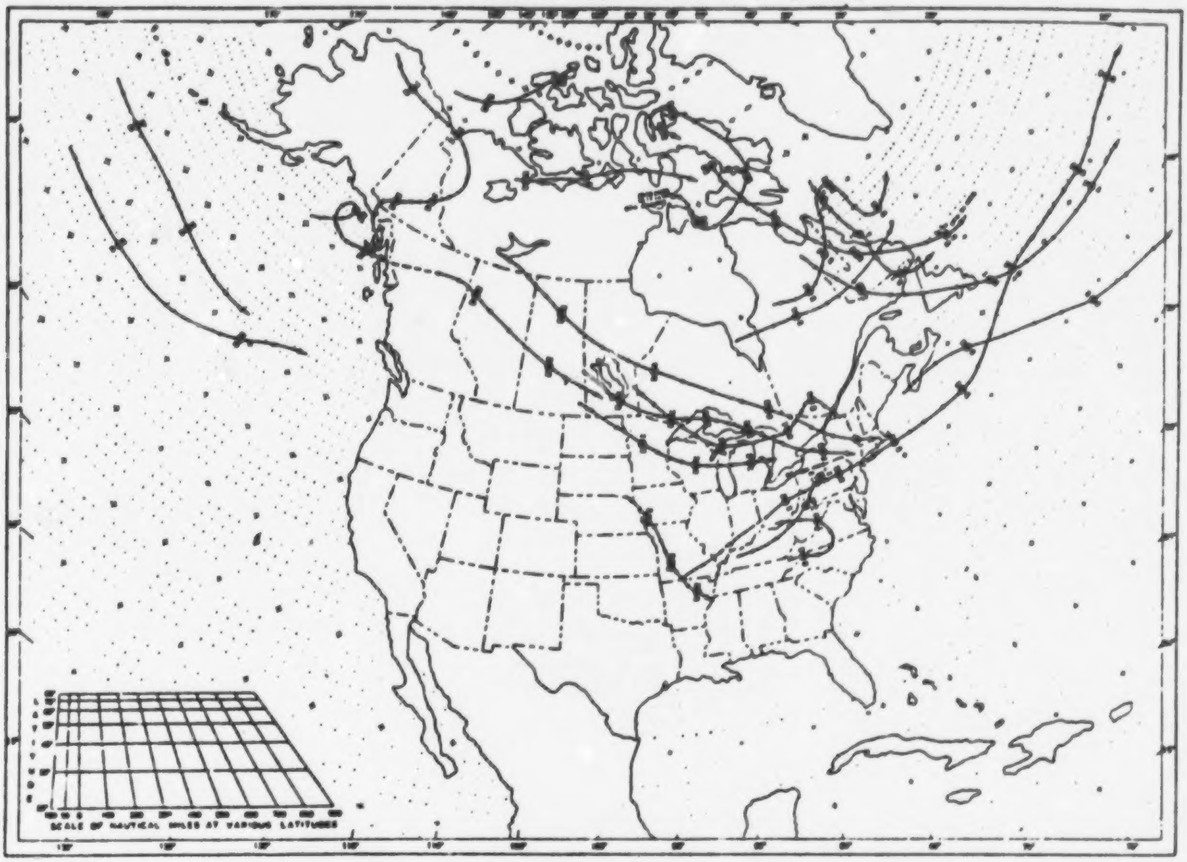
In a postulated sequence of events, a high-pressure system moves into the more populated area holding anthropogenic pollutants in a relatively small volume of air and causing all trace gases with an origin at the surface to accumulate. The influence of a single urban area on the lower layer of the air mass is one of producing a perturbation on and adding an increment to the region-wide pollution system, but this increment loses the identity


UNITED STATES
AVERAGE
57.5
POPULATION PER SQUARE MILE
250 OR OVER
50–249.9
10– 49.9
UNDER 10

Source: U.S. Bureau of the Census, Census of Population and Housing: 1970, United States Summary.

Figure 87. Population density by counties: 1970.

Tracks of Centers of Anticyclones at Sea Level, August 1973



Circle indicates position of center at 7:00 a.m. E.S.T. Figure above circle indicates date, figure below, pressure to nearest millibar. Dots indicate intervening 6-hourly positions. Squares indicate position of stationary center for period shown. Dashed line in track indicates reformation at new position. Only those centers which could be identified for 24 hours or more are included.

Figure 88. Tracks of centers of anticyclones at sea level, August 1973.

of its specific source within 48 to 80 km (30 to 50 miles). In other words, all the air over a very large area becomes polluted to the degree that ozone concentrations in excess of the National Ambient Air Qualtiy Standard (NAAQS) can be generated in sunlight.

As polluted air moves into the area of a sampling station in the afternoon, the ozone concentration is relatively constant throughout the mixing layer. As the sun goes down, photochemical activity drops to zero, and a radiation inversion begins to be established. Ozone is not being generated. In the lowest centimeter of air nearest the ground ozone is being destroyed at a possible rate of $\sim$25 percent hr^{-1}. The effect of this process at any distance aloft depends on meteorological factors. Near the ground, for example, the level of the sample inlet ozone is being destroyed by nitric oxide. These two processes are probably the main ones for destroying ozone in the destructive phase of the diurnal cycle The ozone-depleted air and the ozone-destructive gases diffuse slowly within the radiation inversion and none or very little diffuses above the radiation inversion layer. In the air above the radiation layer, the ozone-destructive materials are near depletion because of the previous day's photochemical primary and secondary activity. Ozone is depleted to a much lesser extent above the radiation layer than at the surface of the ground. Thus, a reservoir of air is maintained at some elevation above the surface in which ozone is at a substantially higher concentration than at the ground. Also, ozone-reactive material is held close to the surface during the time of the radiation inversion.

The morning solar irradiation has two functions in the sequence of events. It warms the surface of the earth and erodes the radiation inversion from the ground up. This mixes air containing higher ozone concentrations downward and carries the accumulated nocturnal emissions of ozone precursors aloft. The second function of the solar irradiation is to initiate photochemical processes. Photochemical generation of ozone proceeds more rapidly near the ground, but due to mixing, the ozone concentration is essentially constant throughout the extended mixing layer by evening.

Computer simulation supports the hypothesis that the concentrations of hydrocarbons and oxides of nitrogen observed may not alone be responsible for the generation of ozone concentrations measured but that an accumulation of stable intermediates produced in the ozone-generative processes upwind will amplify ozone generation from the hydrocarbons and oxides of nitrogen present. Computer simulation also supports the idea that high ozone concentrations (above the NAAQS) can be generated by a mixture of primary precursors (oxides of nitrogen and hydrocarbons) and stable intermediates at concentrations which would not permit such high ozone generation from either the primary precursors alone or the stable intermediates alone.

The trajectory analyses show that the air in which high ozone concentrations occur at the sampling sites has, in 48 hours, come from a few tens to a few hundreds of kilometers away. The sequence of effects, as described above, suggests that diurnal changes in ozone at the ground depend on local processes. The continual generation of high ozone in a sequence of days, as hypothesized above, depends both on transported pollutants as well as hydrocarbons and oxides of nitrogen from local sources.

Our knowledge of the atmospheric behavior of so-called stable intermediates (e.g., RCHO, CH_2O, H_2O_2, HONO) is slight. Whatever their concentration, it seems likely, if the hypothetical sequence of ozone generation and destruction outlined above is correct, that the stable intermediates are destroyed at or near the surface. In that case, the air above the radiation inversion acts as a reservoir of higher concentrations of the intermediates.

7.0 CONCLUSIONS

The following observations and conclusions are based on data collected in the study of high rural concentrations of ozone in 1974 in the eastern United States.

1. The NAAQS for photochemical oxidants was exceeded approximately twice as frequently at the rural stations as at the urban stations. Mean diurnal ozone concentration curves for the rural and urban stations were similar, varying mainly in magnitude of hourly ozone concentration and time of maxima. Nocturnal concentrations of ozone were on the average three to five times higher at the rural sites relative to the urban sites.
2. Nitrogen dioxide concentrations observed at the rural stations were at or near the minimum detectable level for the measurement method (i.e., approximately 10 μg/m^3).
3. There were periods (at times 5 days or more) during which the near surface concentration of ozone equaled or exceeded the NAAQS of 160 μg/m^3 (0.08 ppm) hourly average over large areas (2.3 × 10^5 square kilometers or more). That anthropogenic air pollution was present in this air was demonstrated by the presence of acetylene in all hydrocarbon samples and the presence in a preponderance of samples of carbon monoxide in concentrations 2 to 6 times the usually quoted geochemical background of 91-137 μg/m^3 (0.08 to 0.12 ppm).
4. An area-wide system [radius -240 kilometers (150 miles) or more] of high ozone concentration can exist in which most features suggestive of precursor origin have been smoothed out, but a short-range urban influence on both hydrocarbon and ozone concentrations can be observed. The evidence indicated an observable urban influence extending on the order of 48 to 80 kilometers (30 to 50 miles) downwind of a city.

5. When the central region of a synoptic high pressure system--a region characterized by relatively clear skies and weak, disorganized flow near the surface--moved into the region of interest, high concentrations of ozone, as averaged over all simultaneous cases, were reported at all stations. In this respect, high concentrations of ozone are defined as concentrations in excess of 160 $\mu g/m^3$ for 8 hours each day. This condition persisted as long as the high pressure center remained in the immediate vicinity.
6. Pertinent data from the 1974 summer study show that the high concentrations of ozone observed at rural sites were generated in the lower troposphere.
7. The observed high ozone concentrations cannot be explained in terms of air flow from a specific point source or a single urban-industrial area source. In other words, no specific trajectory could be uniformly associated with the arrival of air containing either high or low concentrations of ozone at any of the rural sites.
8. The results of this research provide substantial support for transport of ozone precursors from urban areas to the rural stations under appropriate meteorological conditions. During transport and in the presence of sunlight, ozone is synthesized.
9. The results of this research program imply that the control of hydrocarbon in any individual city will reduce but not necessarily prevent the occurrence of high rural ozone concentrations in excess of the NAAQS, at any given rural site. The implication is that the release of hydrocarbons and oxides of nitrogen from anthropogenic or biogenic sources, located in either an urban or rural area, all combine to generate appreciable quantities of ozone over wide areas.

8.0 REFERENCES

1. Junge, C. E., Air Chemistry and Radioactivity, Intern. Geophys. Ser., 4, New York, Academic Press. (1963).

2. "Mount Storm, West Virginia-Gorman, Maryland, and Luke, Maryland-Keyser, West Virginia, Air Pollution Abatement Activity", Air Pollution Control Office Publ. No. APTD-0656, Research Triangle Park, N.C., Environmental Protection Agency, April (1971).

3. Richter, H. G., "Special Ozone and Oxidant Measurements in Vicinity of Mount Storm, West Virginia", Final Report, Research Triangle Institute, October (1970).

4. "Investigation of High Ozone Concentration in the Vicinity of Garrett County, Maryland, Maryland and Preston County, West Virginia", Research Triangle Park, N.C., Research Triangle Institute, January (1973). (Also issued as Environmental Protection Agency Report No. EPA-R4-73-019).

5. "Investigation of Ozone and Ozone Precursor Concentrations at Nonurban Locations in the Eastern United States", Research Triangle Park, N.C., Research Triangle Institute, May (1974) (Also issued as Environmental Protection Agency Report No. EPA-450/3-74-034).

6. Decker, C. E., T. M. Royal, and J. B. Tommerdahl, "Field Evaluation of New Air Pollution Monitoring Systems", Final Report. Research Triangle Institute, Contract CPA-70-101, Environmental Protection Agency, June (1972).

7. Lonneman, W. A., S. L. Kopczynski, P. E. Darly, and F. D. Sutterfield, "Hydrocarbon Composition of Urban Air Pollution", Environ. Sci. Technol., 8, 229-236 (1974).

8. Decker, C. E., T. M. Royal, and J. B. Tommerdahl, "Development and Testing of an Air Monitoring System", Final Report. Research Triangle Institute, Contract 68-02-1011, Environmental Protection Agency, December (1973).

9. McKee, H. C., "Collaborative Testing of Methods to Measure Air Pollutants-III Chemiluminescent Method for Ozone". Presented at 67th Annual Meeting of Air Pollution Control Association, Denver, Colorado, June 9-13, 1974.

10. Smith, F. S., T. M. Royal, and C. E. Decker, "Quality Assurance Program Relative to Summer 1974 Oxidant Study", Final Report. Research Triangle Institute, Contract BOA-68-02-1386, Task 8, Environmental Protection Agency, February (1975).

11. Miller, P. R., M. H. McCutchon, and H. D. Milligan, "Oxidant Air Pollution in the Central Valley, Sierra Nevada Foothills, and Mineral King Valley of California", Atmos. Environ., 6, 623 (1972).

12. Stasiuk, W. N. and P. E. Coffey, "Rural and Urban Ozone Relationships in New York State", JAPCA, 24, 564-568 (1974).

13. Bruntz, S. M., W. S. Cleveland, T. E. Graedel, B. Kleiner, and J. L. Warner, "Ozone Concentrations in New Jersey and New York: Statistical Association with Related Variables", Science, 186, 257-258 (1974).

14. Hering, W. S., and T. R. Borden, Jr., "Ozonesonde Observations over North America", Vols, 2, 3, 4, Air Force Cambridge Research Laboratories, Office of Aerospace Research, U.S.A.F. Clearing House, Department of Commerce, Washington, D.C. (1964, 1965, 1967).

15. Kopczynski, S. L., A. P. Altshuller, and F. D. Sutterfield, "Photochemical Reactivities of Aldehyde-Nitric Oxide Systems", Environ. Sci. Technol., 8, 909-918 (1974).

16. Jeffries, H. E. and J. E. Sickles, "Mechanism for Ozone Generation", Personal Communication, January (1975). (Reproduced as table 37.)

APPENDIX A

CALIBRATION SYSTEMS/PROCEDURES

Dynamic calibration procedures were used to calibrate all analyzers used during the field measurement period. Biweekly calibrations were performed on each instrument using the procedures described below.

A-1. General

Because the five stations were at elevations above mean sea level, adjustments to the data were necessary to reduce values to reference condition of 25°C (298K) and 760 mmHg. Adjustments to volume measurements were made using the following equation:

$$V_R = V \times \frac{P}{760} \times \frac{298}{t + 273}$$

where

V_R = volume of air at reference conditions, liters,

V = volume of air at sampling conditions, liters,

P = barometric pressure at sampling conditions, mmHg, and

t = temperature at sampling conditions, °C.

Table A-1 summarizes the sampling conditions assumed for each site.

Table A-1. Altitude-pressure relationship for sampling sites

Station	Altitude above mean sea level		Room temperature, °C	Barometric pressure mmHg	Volume of 1 liter at reference conditions (25°C, 760 mmHg)-liters
	meters	feet			
Wilmington, Ohio	402.5	1,321	25 ± 2°	723.4	0.95
McConnelsville, Ohio	305	1,000	25 ± 2°	732.0	0.96
Wooster, Ohio	346	1,136	25 ± 2°	731.0	0.96
McHenry, Md.	885	2,900	25 ± 2°	682.5	0.90
DuBois, Pa.	554	1.817	25 ± 3°	710.4	0.94

Derived from table p. 9-4, Handbook of Air Pollution, PHS Publication No. 999-AP-44, "Barometric Pressure at Various Altitudes."

Preceding page blank

The same adjusted volume was used each time a calibration was performed. A basic step-wise procedure was employed for dynamic calibration of all air quality analyzers as follows:

1. Verify operational status of each analyzer prior to beginning calibration.
2. Connect instrument inlet line or instrument calibration inlet line, as the case may be, to the manifold of the calibration apparatus or, for hydrocarbon instruments, directly to cylinders containing calibration gas.
3. Allow instrument to sample zero air (i.e., air minus the pollutant of concern) for a period of time sufficient to establish a valid zero output. Average the instrument output for zero input concentration for at least 15 minutes. Record voltage and/or chart readings as dictated by the type of data acquisition system used.
4. Introduce a pollutant calibration concentration equal to approximately 80 percent of the operating range and adjust the span of instrument as required upon initial setup of the instruments. This adjustment is normally required only upon initial setup of an instrument or if excessive span drift occurred during the evaluation period. Omit step 4, except on initial setup of analyzer.
5. Introduce successive pollutant calibration concentrations of 10, 20, 40, 60, and 80 percent of the operating range of the instrument being calibrated. Allow sufficient time to establish a valid instrument output for each calibration concentration, and average the instrument output for that input calibration concentration for at least 15 minutes. Record the voltage and/or chart reading for that calibration point and proceed to the next higher calibration concentration and repeat the sequence of events.
6. Return the instrument inlet line to the ambient air sampling manifold and compute a transfer equation, which relates

pollutant concentration input to instrument voltage output, for each instrument.

7. Document thoroughly all parameters required to complete the calibration record sheet designed for each analyzer.

A-2. Ozone Analyzers

A dynamic calibration system producing ozone by ultraviolet irradiation of oxygen[A-1/] was used to calibrate the gas phase chemiluminescent ozone analyzers. The ozone generator consisted of a shielded mercury lamp (20.3 cm in length) which irradiated clean compressed air flowing through a quartz tube (1.5 cm in diameter). By varying the length of the lamp exposed to the air and the total flow of compressed air (usually set at 5.0 l/min), ozone concentrations from zero to approximately 1 ppm (1960 $\mu g/m^3$) were produced.

A portable calibration unit consisting of a regulated power supply, zero air source, calibrated rotameter, ozone generator, mass flowmeter for nitric oxide mixtures, and a glass manifold with sampling ports was assembled. This unit was transported from site to site for calibration of each ozone (as well as nitrogen dioxide) analyzer. A schematic diagram of the ozone calibration system is shown in figure A-1.

In order to obtain a reference measure of the ozone output of the calibration unit, the neutral-buffered KI analysis method[A-2/] was used for each calibration point. A diagram of the calibration system is shown in figure A-1. The analyzer and the bubbler train sampled simultaneously from the glass manifold. A diagram of the KI sampling train and apparatus used to calibrate the sample flow rate is shown in figure A-2.

A-3. Nitrogen Oxides Analyzer

The NO-NO_2-NO_x analyzer was calibrated by gas phase titration.[A-3/] The technique makes use of the rapid gas phase reaction between NO and O_3 to produce a stoichiometric quantity of NO_2. A schematic diagram showing components of the parts of the calibration size then is presented in figure A-3.

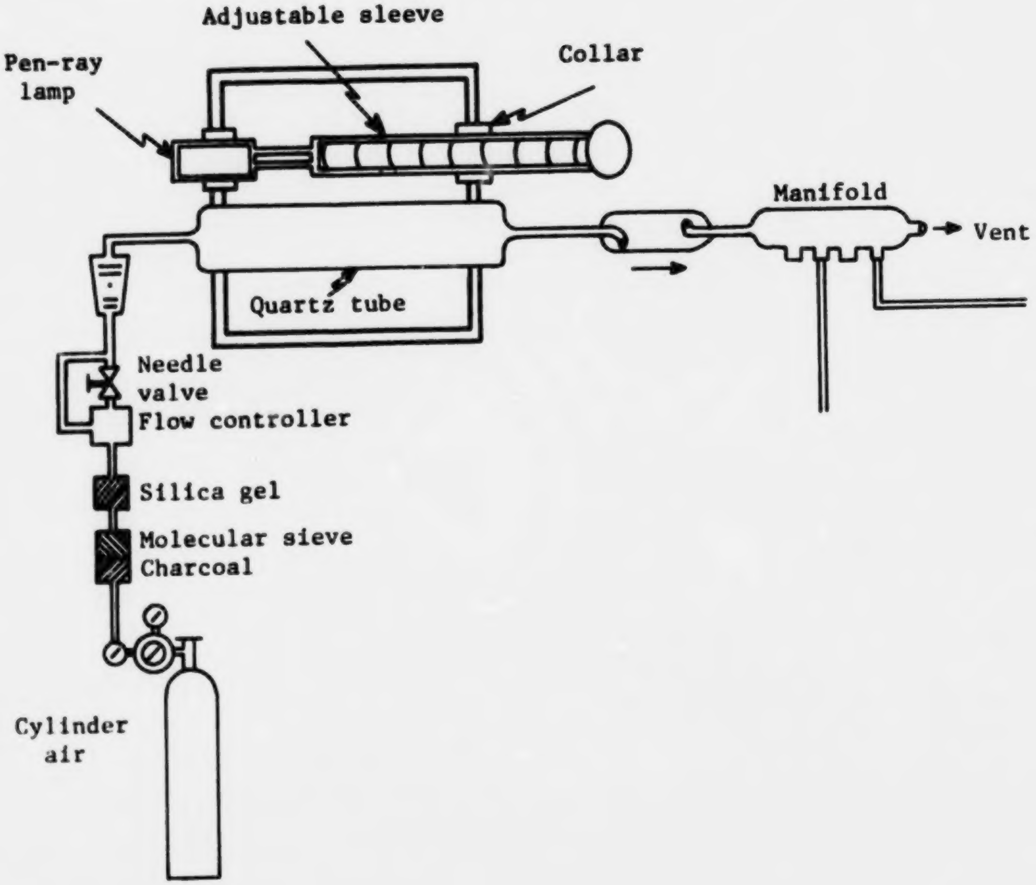

Adjustable sleeve
Pen-ray lamp
Collar
Manifold
Vent
Quartz tube
Needle valve
Flow controller
Silica gel
Molecular sieve
Charcoal
Cylinder air

Figure A-1. Ozone calibration system.

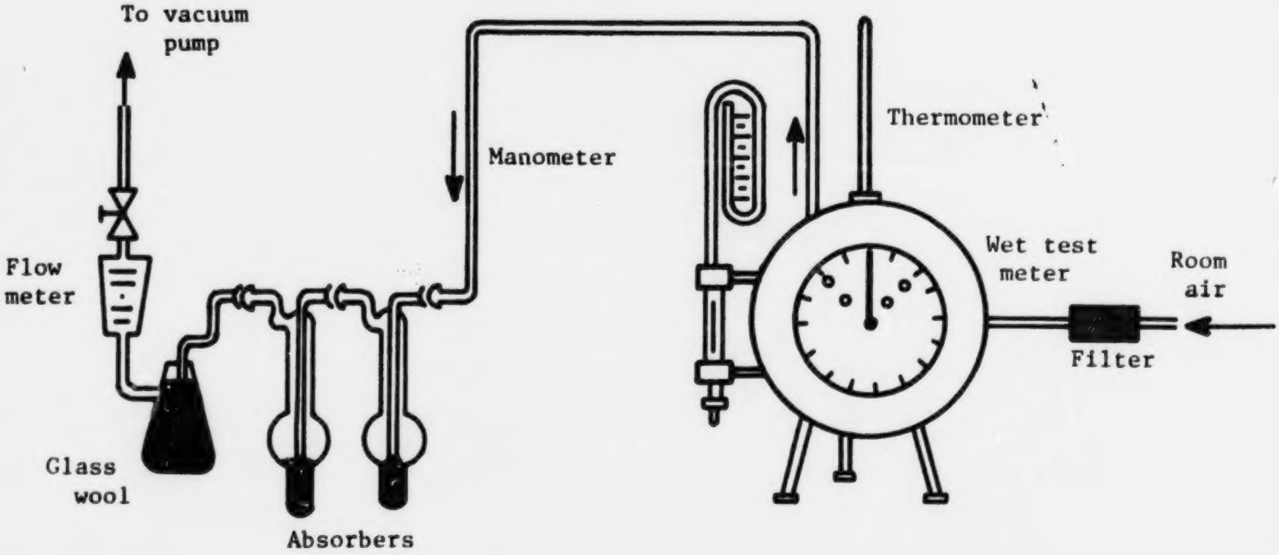

To vacuum pump
Flow meter
Glass wool
Absorbers
Manometer
Thermometer
Wet test meter
Room air
Filter

Figure A-2. KI sampling train and apparatus for calibration of flow rate under operational conditions.

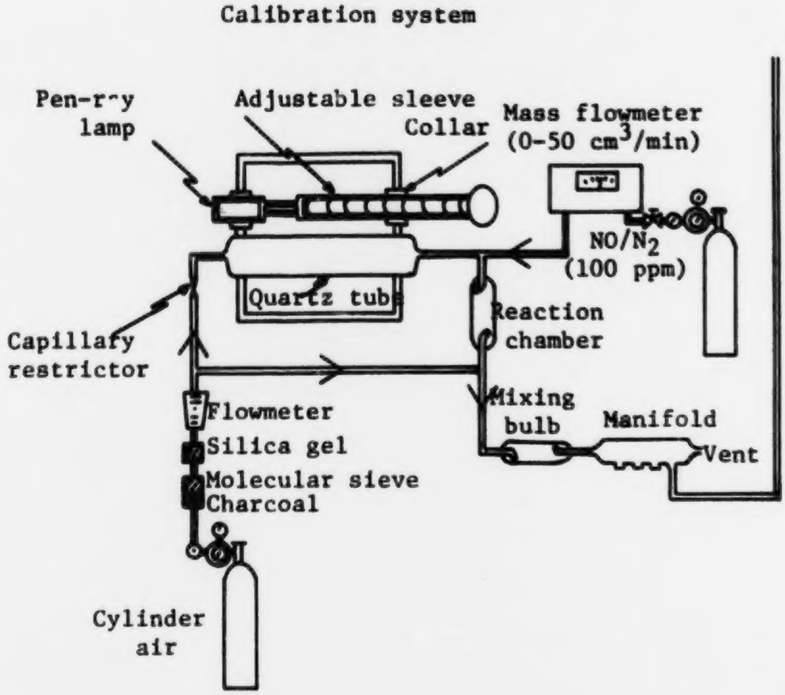

Calibration system
Pen-ray lamp
Adjustable sleeve
Collar
Mass flowmeter
(0-50 cm^3/min)
NO/N$_2$
(100 ppm)
Quartz tube
Reaction chamber
Capillary restrictor
Flowmeter
Silica gel
Molecular sieve
Charcoal
Mixing bulb
Manifold
Vent
Cylinder air

Figure A-3. Gas phase titration system.

After the preliminary zero and span checks, the first step in the final calibration is the introduction of zero air into the analyzer. After 10 minutes, a zero reading is taken on the NO, NO_2, and NO_x channels.

Before transporting the NO calibration gas cylinders to the field, the NO concentration of the contained calibration gases was verified using the technique of Hodgeson and associates.A-3/ The procedure consisted of titrating an NO concentration of 1.0 ppm with successive concentrations of ozone (0-0.8 ppm) produced by an ozone generator referenced to the neutral-buffered KI procedure. The resultant NO detector outputs, after stabilization at each titration points (i.e., 0.0, 0.1, 0.2, ... 0.8 ppm ozone added), were plotted as concentration ppm (y-axis) versus O_3 concentration added, ppm (x-axis). A straight line drawn through the linear portion of the titration curve was extrapolated to the x-axis. The concentration of the x-axis intercept, C_O', was the O_3 concentration equivalent to the initial diluted NO concentration. An example of a typical gas phase titration curve is presented in figure A-4. The cylinder NO concentration was then calculated as follows:
where

C_{NO} = cylinder NO concentration, ppm
F_{NO} = measured NO flow, ml/min,
C_O' = equivalence point O_3, concentration, ppm, and
F_O = total clean air flow, ml/min.

The NO portion of the analyzer was calibrated by dynamic flow dilution of the cylinder gas. This was accomplished by metering the NO from the cylinder through a calibrated mass flowmeter and then into the dilution system of the ozone generator. To calibrate the NO_2 portion of the analyzer, a constant NO concentration of approximately 940 $\mu g/m^3$ (0.5 ppm) was produced by dilution. Ozone was added in increments from the generator. Decrements observed on the spanned NO detector are then equivalent to the NO_2 concentration produced by the O_3 source. Since the NO_2 produced was equivalent to O_3 consumed, the calibrated O_3 source served as a calibrated NO_2 source when NO was present in excess. After adequate time (~10 min)

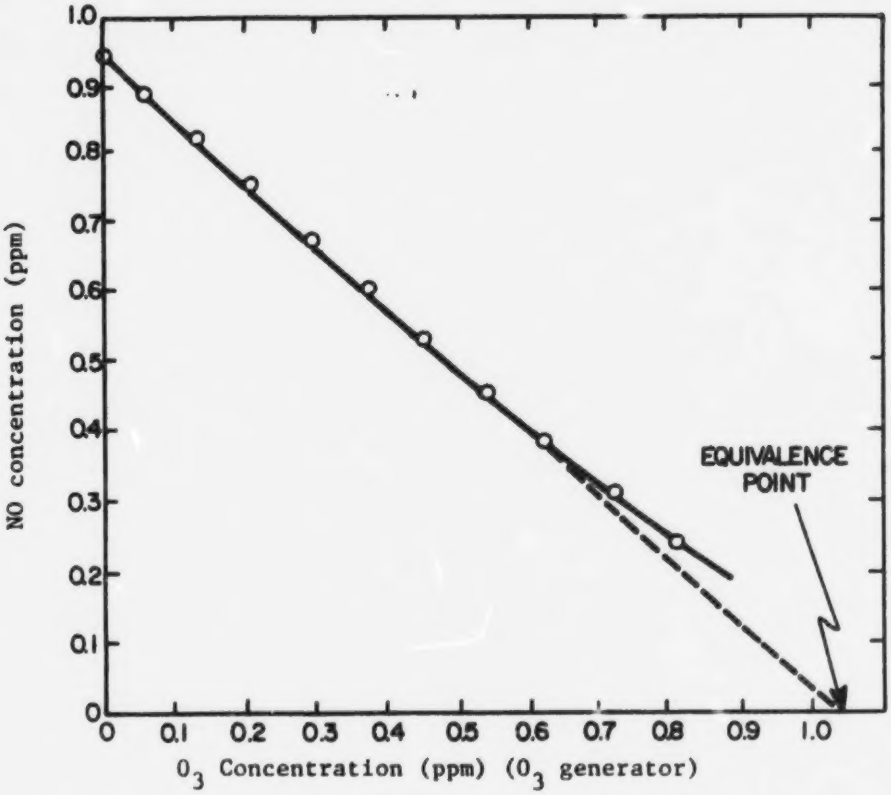


Figure A-4. Gas-phase titration of NO with O_3.

for stabilization at each point, the mV output of each channel was recorded.

The NO_2 concentration was deduced from the decrease of the NO signal, and a calibration curve relating NO_2 concentration and analyzer mV output was constructed.

A-4. Hydrocarbon Analyzer

Calibration of hydrocarbon instruments was accomplished utilizing standard calibration gases certified by the supplier. For this study cylinders of methane in air were obtained from Scott Research Laboratories. Several concentrations ranging from 0 to 10 ppm of CH_4 were used for calibration purposes. In the absence of acceptable cylinders of zero air (i.e., $CH_4 < 0.10$ ppm) an alternate procedure utilizing electronic zeroing was used in lieu of dynamic zero. The following concentrations of methane in air were used to calibrate the hydrocarbon anlyzers:

Supplier	Cylinder #	Certification by manufacturer (± 2%) CH_4*	CO
Scott Research Laboratories Laboratories	A	8.5 ppm	21.4 ppm
	B	8.4 ppm	23.2 ppm
	C	8.1 ppm	24.4 ppm

*THC as CH_4 = CH_4 concentration for cylinders A, B, C.

REFERENCES

A-1. J. A. Hodgeson, R. K. Stevens, and B. E. Martin. "A Stable Ozone Source Applicable as a Secondary Standard for Calibration of Atmospheric Monitors." Air Quality Instrumentation, Vol. 1, John Scales, ed., 149-150, ISA, Pittsburgh, Pa., 1972.

A-2. 40 CFR 50, Appendix D.

A-3. J. A. Hodgeson, R. E. Baumgardner, B. E. Martin, and K. A. Rehme. "Stoichiometry and Neutral Iodometric Procedure for Ozone by Gas-Phase Titration with Nitric Oxide." Anal. Chem. 43. 1123-1126, 1971.

APPENDIX B

PERFORMANCE CHARACTERISTICS AND OPERATIONAL SUMMARIES FOR INSTRUMENTS

B-1. Instrument Performance Characteristics.

Minimum detectable concentrations, ranges, and precisions for the air quality monitoring instruments used in this study are summarized in table B-1.

B-2. Operational Summaries for Instruments by Station.

Operational data are summarized for each analyzer by station during this study in table B-2. For this program, operational time is divided into the following categories:

(1) Percent operational time, and

(2) Percent downtime.

Percent operational time includes all categories or operational status other than downtime, which includes routine maintenance, awaiting repair, or repair. The data presented in table B-2 include percent operational time--which is synonymous with percent valid data--percent downtime, and number and nature of failures. It should also be noted that, for this study, Research Triangle Institute engineers and technicians were responsible for maintenance and repair of all analyzers, except the Beckman Model 6800 THC, CH_4, CO analyzers. Beckman, under separate contract to the Chemistry and Physics Laboratory of Environmental Protection Agency, supplied three Model 6800 chromatographs with calibration gases, etc., and was responsible for maintenance and/or repair of the Beckman analyzers. Included in the service contract were labor, parts, routine maintenance/calibration at 2-week intervals, and 24-hour turnaround on service for instrument failure.

Preceding page blank

Table B-1. Instrument performance characteristics

Instrument	Parameter	Minimum detectable concentration		Range		Precision (% of indicated concentration)
		μg/m^3	ppm	μg/m^3	ppm	
Bendix Model 8002 Chemiluminescent Ozone Analyzer	O_3	4.0	0.002	0-392	0-0.2	± 2%
RTI Solid Phase Chemiluminescent Ozone Analyzer	O_3	4.0	0.002	0-392	0-0.2	± 2%
Bendix Model 8101-B Chemiluminescent NO-NO_x-NO_2 Analyzer	NO, NO_x NO_2	9.4	0.005	0-940	0-0.5	± 2%
Beckman Model 6800 THC, CH_4, CO Analyzer	THC, CH_4, CO	30.0	0.050	0-3270	0-5.0	± 2%
Perkin-Elmer Model 900 Gas Chromatograph	Selected Hydrocarbons	sub-ppb		ppb-ppm		± 1%

Table B-2. Operational summary for instruments by station

Station	Instrument	Operational period (days)	Operational time (%)	Downtime (%)	Failure	Nature of Failure
Wilmington, Ohio	Bendix O_3	80	87.5	12.5	2	a
	Bendix NO_x	79	87.3	12.7	2	a
	Beckman THC, CH_4, CO	79	33.0	67.0	7	a, b, c, d
McConnelsville, Ohio	Bendix O_3	76	97.4	2.6	1	e
	Bendix NO_x	76	95.0	5.0	1	e
	Beckman THC, CH_4, CO	62	61.0	39.0	3	b, c, d, e
Wooster, Ohio	Bendix O_3	78	100.0	0	0	---
	Bendix NO_x	78	100.0	0	0	---
	Beckman THC, CH_4, CO	73	41.0	59.0	9	b, c, d, e
McHenry, Maryland	Bendix O_3	79	100.0	0.0	0	---
	Bendix NO_x	79	100.0	0.0	0	---
DuBois, Pennsylvania	Bendix O_3	79	87.9	12.1	1	c
	Bendix NO_x	79	100.0	0.0	0	---
Canton, Ohio*	Bendix O_3	79	88.6	11.4	1	g
Cincinnati, Ohio*	Bendix O_3	79	81.0	19.0	1	c, e
Cleveland, Ohio*	Bendix O_3	79	87.3	12.7	1	g
Columbus, Ohio*	Bendix O_3	79	98.0	2.0	0	c
Dayton, Ohio*	Bendix O_3	79	83.5	16.5	2	c, e
Pittsburgh, Pennsylvania*	Bendix O_3	79	86.0	14.0	1	e

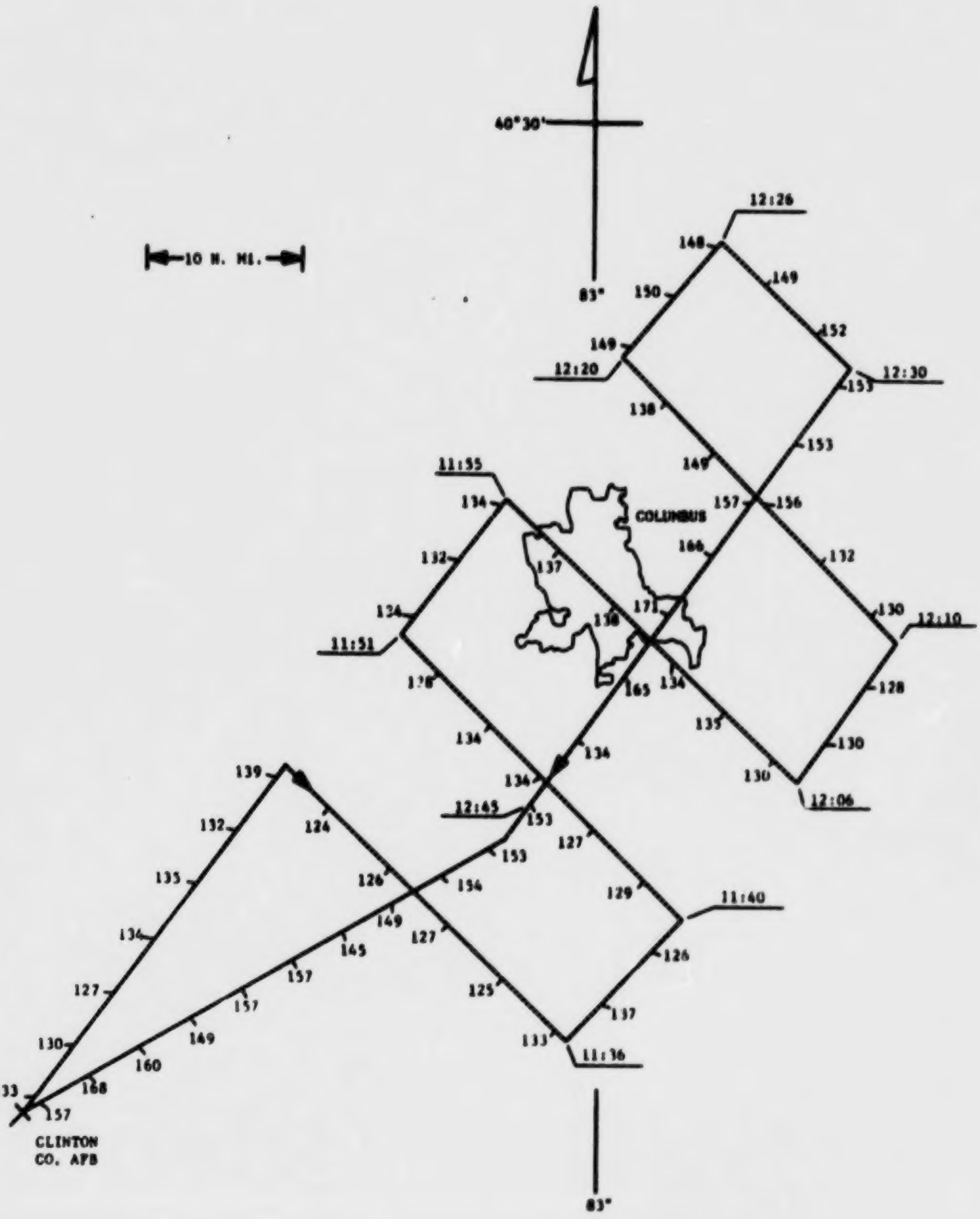
*Urban stations
a - Power failure
b - Flame-out
c - Flow system problem
d - Leak in air supply system
e - Electronic circuitry problem
f - Detector cell failure
g - Excessive zero/span drift

APPENDIX C

AIRCRAFT FLIGHT PLANS/DATA/ METEOROLOGICAL SUMMARY FOR EACH FLIGHT

LISTING OF AIRCRAFT FLIGHTS

Figure number	Date	Pattern	Times	Flight altitude (meters)
C-1	20 June	Square Wave	1126--1245	610
C-2	25 June	Vertical Profile	0754--0934	to 3658
C-3	27 June	Square Wave	1131--1340	762
C-4	4 July	Square Wave	1148--1256	762
C-5	6 July	Double Box	1245--1719	762
C-6	9 July	Double Box	1026--1449	762
C-7	13 July	Double Box	1100--1518	762
C-8	16 July	Square Wave	1130--1403	914
C-9	17 July	Vertical Profile	1155--1321	to 2590
C-10	21 July	Square Wave	1158--1434	975
C-11	25 July	Square Wave	1308--1622	762
C-12	1 Aug	Vertical Profile	0704--0810	to 2438
C-13	1 Aug	Vertical Profile	0823--0913	to 1829
C-14	1 Aug	Vertical Profile	1320--1414	to 3658
C-15	1 Aug	Vertical Profile	1656--1822	to 3658
C-16a	9 Aug	Batelle Comparison Flight	1502--1631	610
C-16b	9 Aug	Batelle Comparison Flight	1546--1630	610
C-17	13 Aug	Vertical over Morgan and Wayne County	1024--1406	762 to 2286
C-18	15 Aug	Vertical Profile	1053--1218	366
C-19	21 Aug	Eastern Flight	0939--1632	1219


40°30'
83°
10 N. MI.
12:26
148
149
150
149
152
12:20
12:30
153
138
153
149
11:55
157
156
134
COLUMBUS
166
132
132
137
171
130
12:10
134
138
11:51
128
165
134
128
135
130
134
134
130
12:06
139
134
12:45
153
132
124
127
153
135
126
134
129
11:40
149
136
145
127
157
126
127
157
125
137
149
130
160
133
11:36
133
168
157
CLINTON
CO. AFB
83°

FLIGHT DATE: June 20, 1974

PATTERN: Square Wave

TRUE AIRSPEED: 277.8 km/h (150 knots)

MISSION ALTITUDE: 609.6 m (2,000 ft) above msl

LOW LEVEL WINDS:	
Sfc	215°/2.57 m/s (5 knots)
609 m (2,000')	270°/9.26 m/s (18 knots)
914 m (3,000')	300°/9.77 m/s (19 knots)
1219 m (4,000')	290°/10.29 m/s (20 knots)

DATA: Ozone Concentration in ug/m^3
Time in EDT

Figure C-1. Partial square wave flight on June 20, 1974.

Flight Data - June 20, 1974

Square Wave

Time	Leg	O_3*	NO_2*	Temp. (°C)
1105	Base	133		
		130		
		127		
		134		
		135		
		132		
1126	1	124	17	26.7
		126		
		127		
		125		
		133		
1136	2	137	17	26.1
		126		
1141	3	129	17	26.1
		127		
		134		
		134		
		128		
1151	4	134	17	26.6
		132		
		134		
1156	5	137	34	26.4
		138		
		134		
		135		
		130		
1206	6	130	34	26.4
		128		
1211	7	130	34	26.4
		132		
		156		
		149		
		138		
1221	8	149	17	26.7
		150		
		148		
	9	149	17	26.7
		152		
1231	10	153		
		153		
		157		
		166		
		171		
		171		
		165		
		153		
1245	11	153		
		154		
		149		
		145		
		157		
		157		
		149		
		160		
		168		
		157		
		149		
		145		
		157		

- Nitric oxide below detectable limit.

*Concentration in $\mu g/m^3$.

METEOROLOGICAL SUMMARY FOR FLIGHT

High pressure centered over northern Alabama produced moderately strong westerly flow through Ohio. Winds at the 2000 foot msl flight level were 280° at 20 knots. Flight level visibility was generally less than 5 miles.

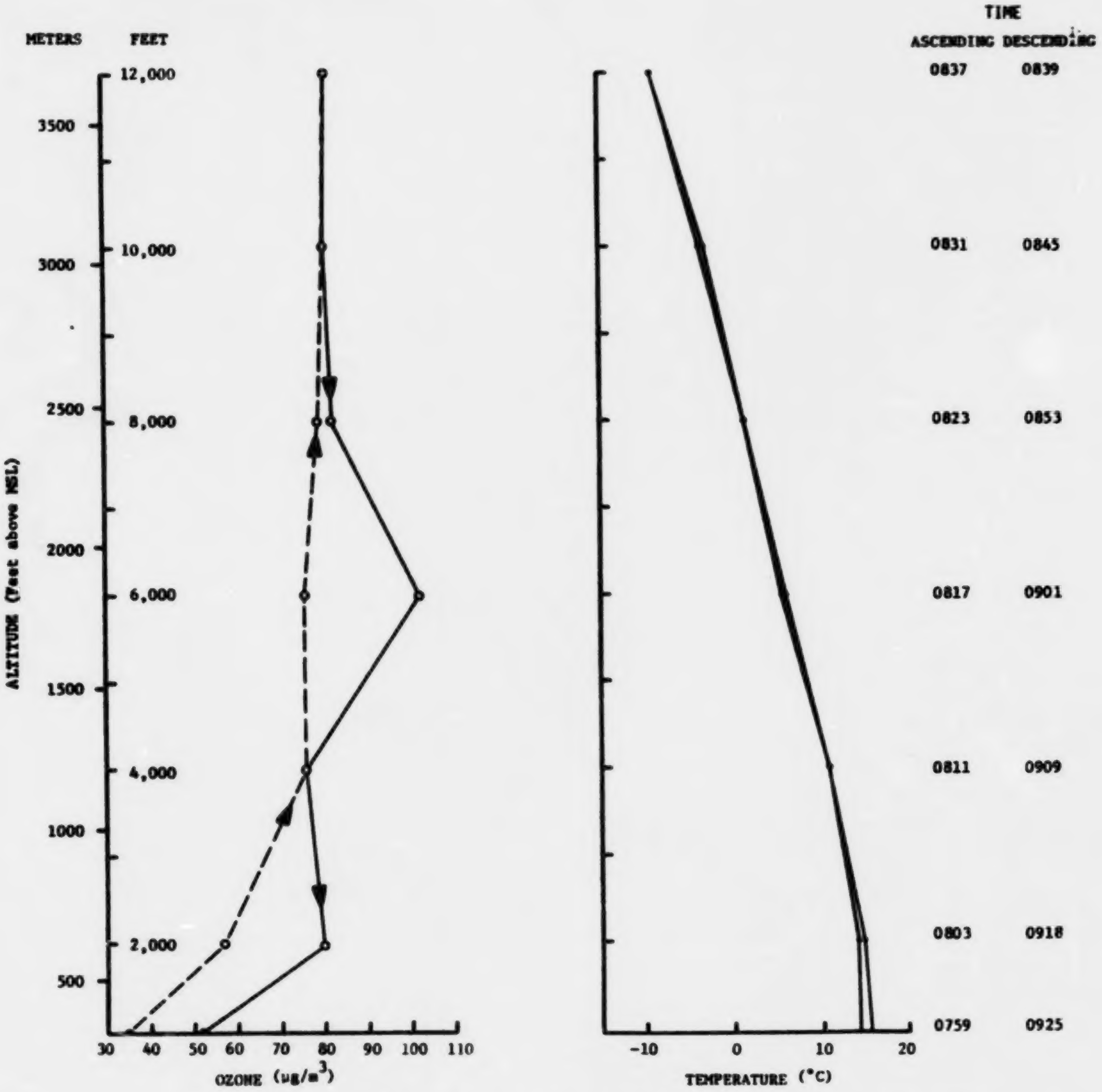
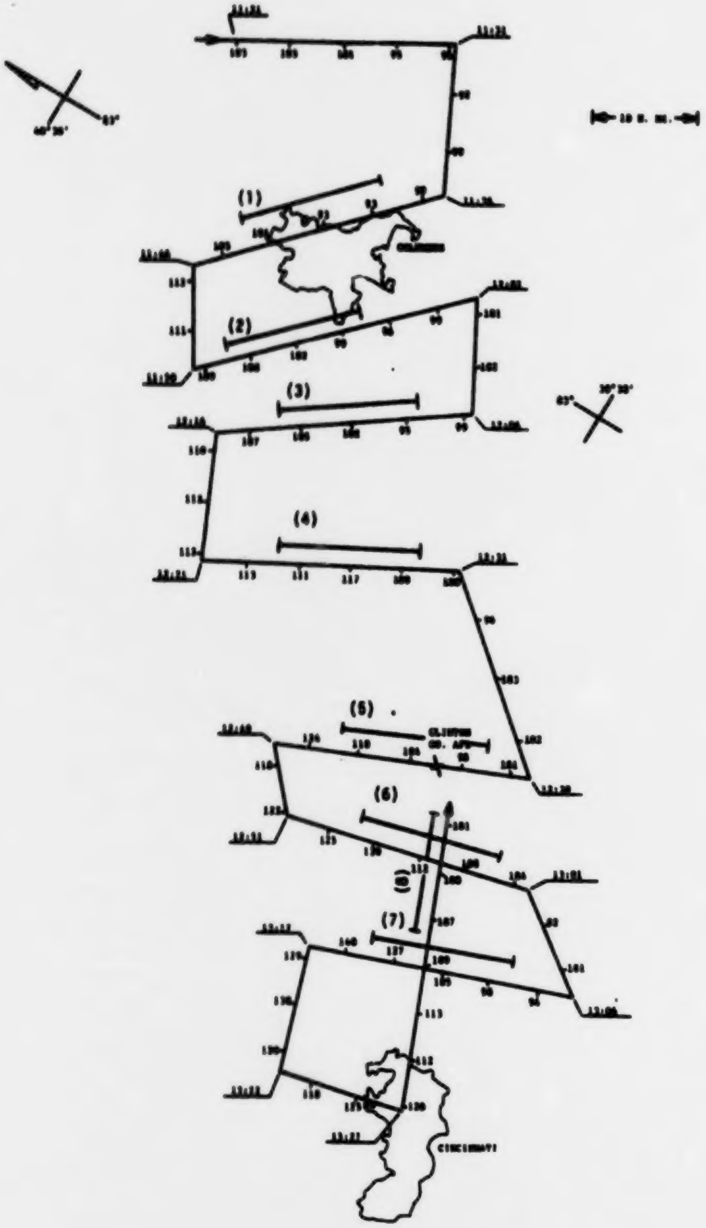


Figure C-2. Vertical profile flight on June 25, 1974.

Flight Data - June 25, 1975

Vertical Profile - Wilmington, Ohio

Time	Altitude (Meters)	O_3 ($\mu g/m^3$)	Temp. (°C)	NO/NO_2 ($\mu g/m^3$)
0803	610	57	12.5	below detectable
0811	1220	76	7.7	
0817	1830	76	3.0	
0823	2440	79	- 1.1	
0831	3050	80	- 5.5	
0837	3660	81	- 5.5	
0845	3050	80	- 0.5	
0853	2440	82	3.0	
0901	1830	102	8.4	
0909	1220	76	12.9	
0918	610	80	15.0	



FLIGHT DATE: June 27, 1974

TRUE AIRSPEED: 277.8 km/h (150 knots)

PATTERN: Square Wave

MISSION ALTITUDE: 762.0 m (2,500 ft) above msl

LOW LEVEL WINDS:

Sfc	070°/5.14 m/s (10 knots)
609 m (2,000')	080°/8.74 m/s (17 knots)
914 m (3,000')	065°/8.23 m/s (16 knots)
1219 m (4,000')	055°/7.72 m/s (15 knots)

DATA: Ozone Concentration in $\mu g/m^3$
Time in EDT

Hydrocarbon Sample Positions
Denoted by ├──────┤

Low Level Winds From
National Weather Service
Upper Air Station
Dayton, Ohio-0800 EDT

Figure C-3. Partial square-wave flight on June 27, 1974.

Flight Data - June 27, 1974

Square Wave

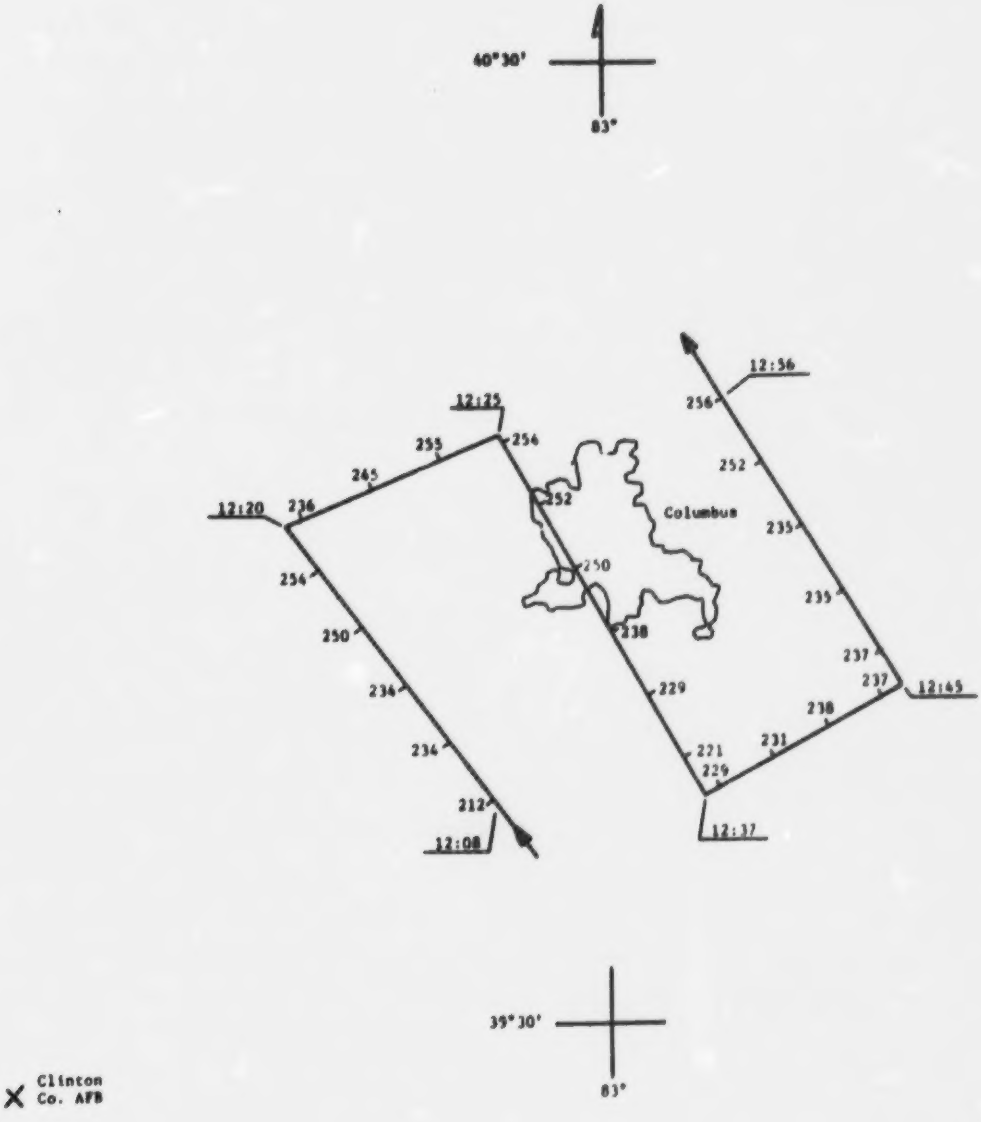
Time	Leg	O_3*	Temp. (°C)
1121	Base	138	15.8
		138	
		135	
		127	
		127	
1131	1	123	15.9
		133	
1136	2	133	16.1
		125	
		125	
		135	
		141	
1146	3	150	16.8
		149	
1150	4	146	16.2
		145	
		137	
		133	
		129	
		133	
1202	5	135	16.2
		137	
1207	6	133	16.3
		127	
		137	
		141	
		143	
1217	7	147	16.3
		150	
		150	
1222	8	151	16.7
		149	
		157	
		146	
		134	
1232	9 9	129	16.6
		138	
		137	
1239	10	135	16.3
		131	
		139	
		147	
		166	
1249	11	158	17.4
		163	
1252	12	168	17.3
		174	
		150	
		145	
		139	
1302	13	123	
		135	
1307	14	126	
		131	
		141	
		170	
		188	
1317	15	173	17.3
		174	
		161	
1322	16	158	16.7
		168	
RETURN		161	
		150	
		151	
		146	
		143	
		134	
		135	

- Nitrogen dioxide and nitric oxide below detectable limit

* Concentration in $\mu g/m^3$.

METEOROLOGICAL SUMMARY FOR FLIGHT OF JUNE 27, 1974

A high pressure center over Quebec produced a northeasterly flow over Ohio. Winds at the 2500 foot msl flight level were 060° at 15 knots. There was scattered cumulus at 3000 feet msl. Good VFR visibility was maintained throughout the mission with good thermal mixing to 9000 feet msl.


40°30'
83°
12:25
12:36
256
255
254
245
252
12:20
236
Columbus
235
254
250
235
250
238
237
237
12:45
234
229
238
231
234
221
229
212
12:08
12:37
39°30'
83°
Clinton
Co. AFB

FLIGHT DATE: July 4, 1974

PATTERN: Square Wave

TRUE AIRSPEED: 240.8 km/h (130 knots)

MISSION ALTITUDE: 762.0 m (2,500 ft) above msl

LOW LEVEL WINDS:	
Sfc	220°/3.60 m/s (7 knots)
609 m (2,000')	225°/13.9 m/s (27 knots)
916 m (3,000')	240°/15.4 m/s (30 knots)
1219 m (4,000')	245°/14.9 m/s (29 knots)

DATA: Ozone Concentration in ug/m^3
Time in EDT

Figure C-4. Partial square-wave flight on July 4, 1974.

Flight Data - July 4, 1974

Square Wave

Time	Leg	O_3*	Temp. (°C)	Time	Leg	O_3*	Temp. (°C)
1208	Base	212	26.3	1238	3	229	26.3
		234				231	
		234				238	
		250				237	
		254					
				1245	4	237	
1220	1	236	26.5			235	
		245				235	
		255				252	
						256	
1226	2	254	26.3				
		252		1257	ABORT		
		250					
		238					
		229					
		221					

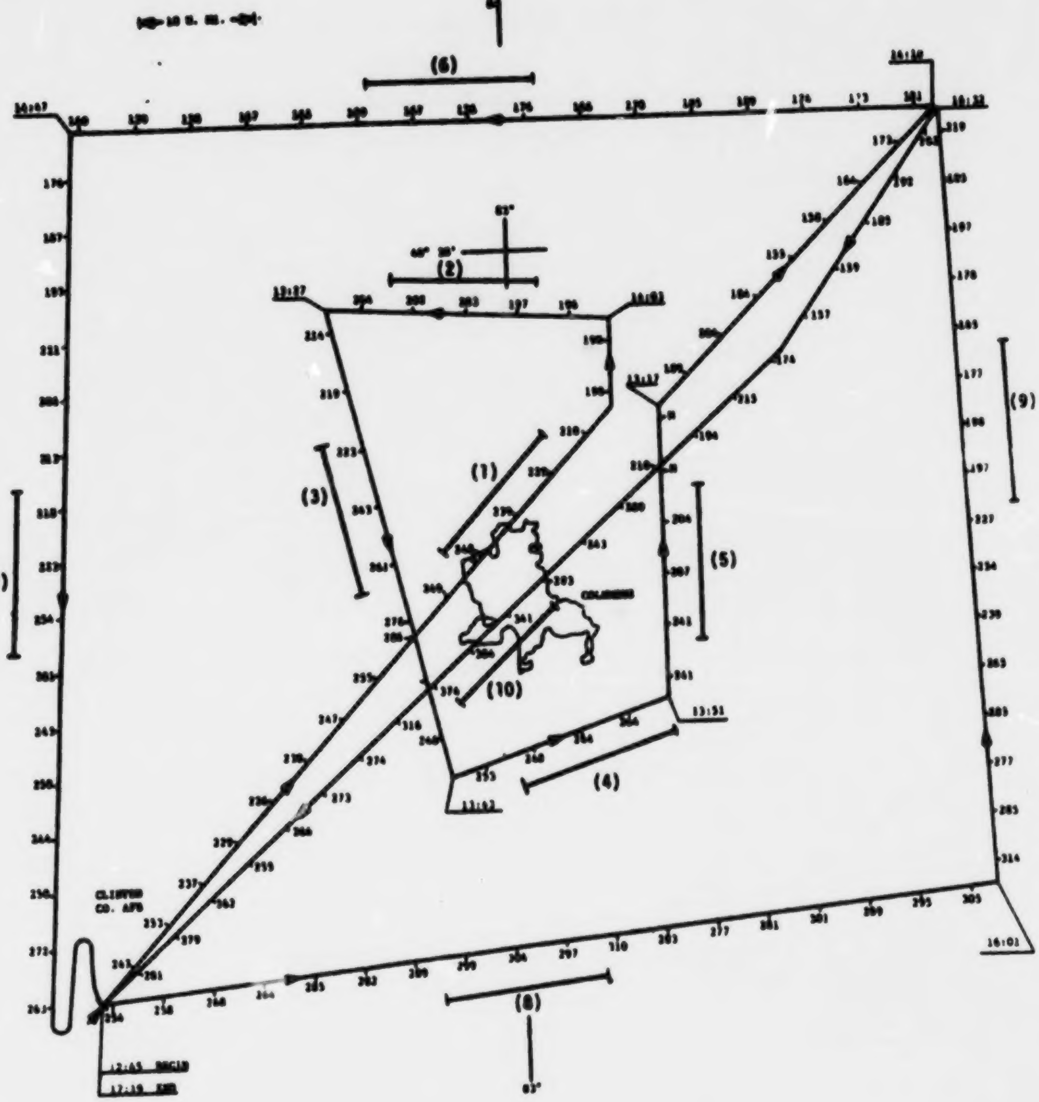
- Nitrogen dioxide and nitric oxide below detectable limits

* Concentration in $\mu g/m^3$.

METEOROLOGICAL SUMMARY FOR FLIGHT

Strong low level southwesterly flow predominated with winds at the 2500 foot msl flight level being 235° at 28 knots. Scattered cumulus formed at 3500 feet msl below which it was moderately hazy. Thermal mixing in the afternoon extended through a layer up to 8500 feet msl.

4


(1)
(2)
(3)
(4)
(5)
(6)
(7)
(8)
(9)
(10)
14:07
16:10
16:32
13:27
14:03
13:17
13:51
13:42
16:01
12:45 BEGIN
17:19 END
CLINTON CO. AFB
COLUMBUS
83°
40° 30'

FLIGHT DATE: July 6, 1974

TRUE AIRSPEED: 277.8 km/h (150 knots)

PATTERN: Double Box

MISSION ALTITUDE: 762.0 m (2,500 ft) above msl

LOW LEVEL WINDS:

Sfc	080°/2.57 m/s (5 knots)
609 m (2,000')	130°/3.60 m/s (7 knots)
914 m (3,000')	215°/2.06 m/s (4 knots)
1219 m (4,000')	290°/2.06 m/s (4 knots)

DATA: Ozone Concentration in μg/m^3
Time in EDT
Hydrocarbon Sample Positions
Denoted by ├────────┤.

Low Level Winds From
National Weather Service
Upper Air Station
Dayton, Ohio—0800 EDT

Figure C-5. Double-box flight of July 6, 1974.

Flight Data - July 6, 1974

Double-Box

Time	Leg	O_3*	Temp. (°C)
1245	Base	247	23.0
		253	
		237	
		229	
		226	
		237	
		247	
		255	
		286	
		249	
		248	
		239	
		229	
		210	
		198	
		198	
1317	1	196	22.3
		197	
		203	
		202	
		204	
1327	2	214	22.5
		219	
		223	
		243	
		261	
		276	
		257	
		246	
1343	3	253	23.5
		248	
		244	
		264	
1351	4	241	22.5
		241	
		207	
		204	
1403	4A	189	21.8
		204	
		184	
		155	
		158	
		164	
		173	
1418	5	181	23.7
		173	
		174	
		189	
		185	
		178	
		166	
		176	
		167	
		169	
		165	
		167	
		158	
		159	
		160	
1447	6	176	24.7
		187	
		197	
		221	
		206	
		213	
		218	
		223	
		254	
		281	
		245	
		250	
		244	
		250	
		272	
		263	

- Nitrogen dioxide and nitric oxide below detectable limits.

* Concentration in $\mu g/m^3$.

Flight Data - July 6, 1974

Double-Box (Continued)

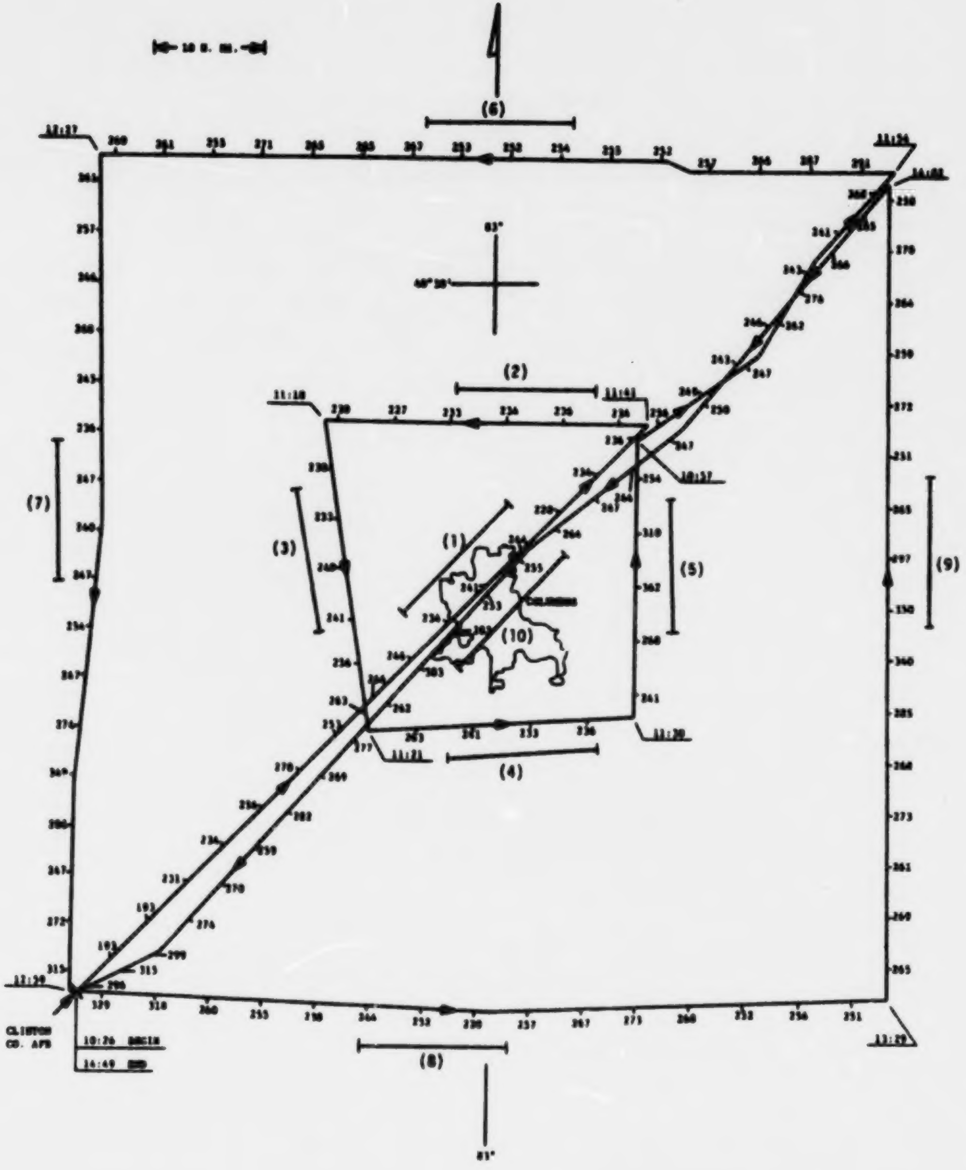
Time	Leg	O_3*	Temp. (°C)	Time	Leg	O_3*	Temp. (°C)
1525	7	254	25.5	1632	9	202	25.0
		258				192	
		268				185	
		264				159	
		285				157	
		282				174	
		289				215	
		299				194	
		304				210	
		297				209	
		310				243	
		283				283	
		277				341	
		281				384	
		301				374	
		289				316	
		295				274	
		305				273	
						266	
1601	8	314	24.4			255	
		285				262	
		277				279	
		285				281	
		265					
		239		1719	END		26.8
		254					
		227					
		197					
		198					
		177					
		165					
		178					
		197					
		185					
		219					

- Nitrogen dioxide and nitric oxide below detectable limits.

* Concentration in $\mu g/m^3$.

METEOROLOGICAL SUMMARY FOR FLIGHT OF JULY 6, 1974

A high pressure center over lake Erie sitting behind a dissipating stationary front over the Ohio River Valley divided the mission area in half along an east-west line through Columbus. The northern sector was clear with unlimited visibility. Visibility in the southern sector was sometimes less than ½ mile due to heavy haze. The transition area between these two sectors was less than ten miles across. Winds up through the 2500 foot msl flight altitude were light and veering in direction. Thermal mixing was indicated up to 8000 feet msl.


10 n. mi.
(1)
(2)
(3)
(4)
(5)
(6)
(7)
(8)
(9)
(10)
83°
40°30'
11:27
11:54
14:02
11:18
11:41
10:57
11:21
11:30
12:39
13:29
COLUMBUS
CLINTON
CO. AFB
10:26 BEGIN
14:49 END

FLIGHT DATE: July 9, 1974

TRUE AIRSPEED: 277.8 km/h (150 knots)

PATTERN: Double Box

MISSION ALTITUDE: 762.0 m (2,500 ft) above msl

LOW LEVEL WINDS: Sfc	215°/2.06 m/s (4 knots)
609 m (2,000')	250°/4.63 m/s (9 knots)
914 m (3,000')	270°/3.09 m/s (6 knots)
1219 m (4,000')	285°/2.57 m/s (5 knots)

DATA: Ozone Concentration μg/m^3
Time in EDT
Hydrocarbon Sample Positions
Denoted by ├──────┤

Low Level Winds From
National Weather Service
Upper Air Station
Dayton, Ohio-0800 EDT

Figure C-6. Double-box flight on July 9, 1974.

Flight Data - July 9, 1974

Double-Box

Time	Leg	O_3*	Temp. (°C)	Time	Leg	O_3*	Temp. (°C)
1027	Base	193	26.4	1141	4A	256	26.8
		193				249	
		231				243	
		234				246	
		256				243	
		270				241	
		253				268	
		266					
		246		1154	5	291	27.5
		234				287	
		241				266	
		244				257	
		220				252	
		234				255	
		236				254	
						252	
1057	1	234	26.3			253	
		236				267	
		234				265	
		233				265	
		227				271	
		230				255	
						261	
1110	2	230	26.4			260	
		233					
		240		1227	6	261	27.4
		241				257	
		256				246	
		263				260	
						245	
1121	3	263	26.5			236	
		241				247	
		233				240	
		236				247	
						274	
1130	4	241				349	
		268				286	
		362				247	
		310				272	
		254				315	

- Nitrogen dioxide and nitric oxide below detectable limits.

* Concentration in μg/m^3.

Flight Data - July 9, 1974

Double-Box (Continued)

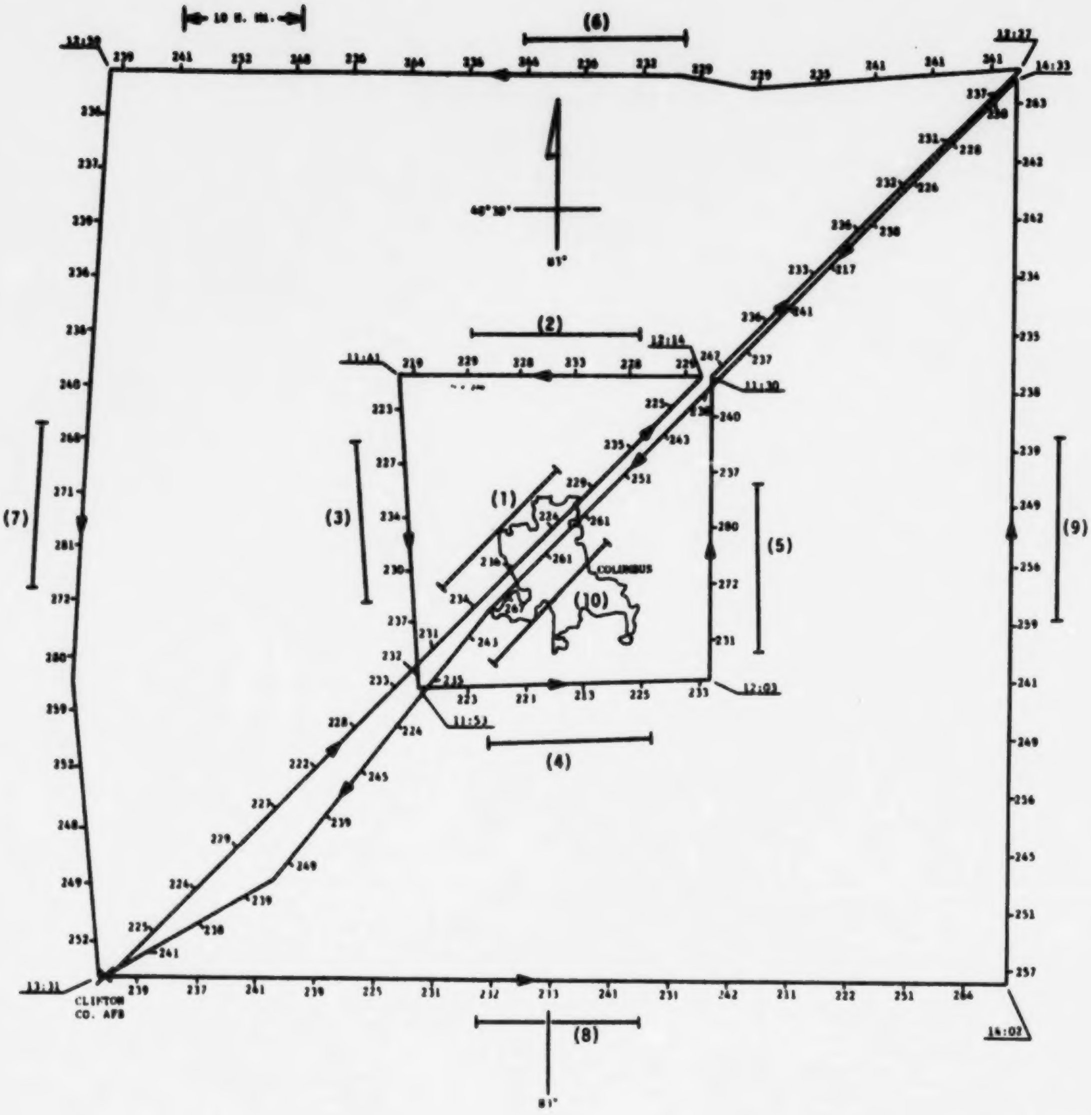
Time	Leg	O_3*	Temp. (°C)	Time	Leg	O_3*	Temp. (°C)
1259	7	329	27.5	1402	9	265	28.0
		318				266	
		260				276	
		255				262	
		238				247	
		244				250	
		252				247	
		220				244	
		257				247	
		267				264	
		273				255	
		268				253	
		252				282	
		256				303	
		251				262	
						277	
1329	8	265	27.7			269	
		269				282	
		261				259	
		273				270	
		268				274	
		285				299	
		340				315	
		350				296	
		297					
		265		1449	END		28.4
		251					
		272					
		259					
		264					
		270					
		258					

- Nitrogen dioxide and nitric oxide below detectable limits.

* Concentration in μg/m^3.

METEOROLOGICAL SUMMARY FOR FLIGHT

This was the third day of stagnant high pressure with the center now located over southeastern Kentucky producing a light generally westerly flow over the mission area. Visibility at 2500 feet msl was 2 to 4 miles throughout the flight. Cumulus formed at 3000 feet msl with thermal mixing occurring to 9300 feet msl.


10 n. mi.
12:39
12:27
14:33
13:31
14:02
11:41
12:14
11:30
12:03
11:53
40°30'
81°
(1)
(2)
(3)
(4)
(5)
(6)
(7)
(8)
(9)
(10)
COLUMBUS
CLIFTON
CO. AFB

FLIGHT DATE: July 13, 1974
TRUE AIRSPEED: 250.0 km/h (135 knots)

PATTERN: Double Box
MISSION ALTITUDE: 762.0 m (2,500 ft) above msl

LOW LEVEL WINDS:	
Sfc	130°/2.06 m/s (4 knots)
609 m (2,000')	205°/3.09 m/s (6 knots)
914 m (3,000')	145°/1.03 m/s (2 knots)
1210 m (4,000')	075°/1.03 m/s (2 knots)

DATA: Ozone Concentration in μg/m^3
Time in EDT
Hydrocarbon Sample Positions Denoted by |———|

Low Level Winds From
National Weather Service
Upper Air Station
Dayton, Ohio-0800 EDT

Figure C-7. Double box flight on July 13, 1974.

Flight Data - July 13, 1974

Double-Box

Time	Leg	O_3*	Time	Leg	O_3*	Time	Leg	O_3*
1100	Base	225	1203	4	231	1259	6	236
		224			272			237
		229			280			239
		227			237			236
		222			240			236
		228						240
		233	1214	4A	247			268
		231			236			271
		234			233			281
		236			236			272
		224			232			280
		229			231			259
		235			237			252
		225						248
			1227	5	241			249
1130	1	229			241			252
		228			241			
		233			235	1331	7	239
		228			229			237
		229			229			241
		219			232			239
					236			225
1142	2	223			244			231
		227			236			232
		234			248			233
		230			252			241
		237			241			231
		232			239			242
								211
1154	3	223						222
		223						251
		213						264
		225						
		233						

- Nitrogen dioxide and nitric oxide below detectable limits.

* Concentration in $\mu g/m^3$.

Flight Data - July 13, 1974

Square Wave

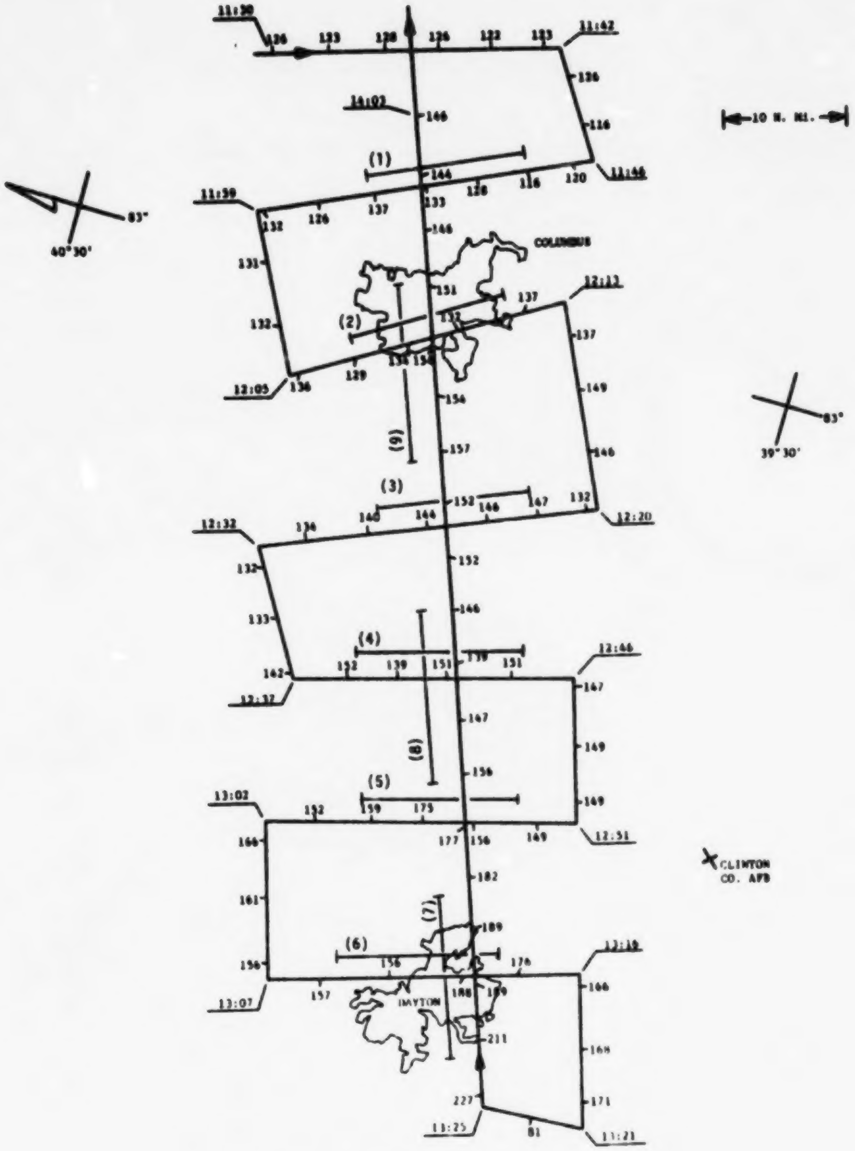
Time	Leg	O_3*	Time	Leg	O_3*
1402	8	257	1433	9	258
		251			228
		245			226
		256			238
		249			217
		241			241
		259			237
		256			238
		249			243
		239			251
		238			261
		235			261
		234			267
		242			243
		242			235
		263			224
					245
					239
					249
					239
					238
					241
			1518	END	

- Nitrogen dioxide and nitric oxide below detectable limits.

* Concentration in $\mu g/m^3$.

METEOROLOGICAL SUMMARY FOR FLIGHT

A high center over the Ohio Valley produced light winds which backed from southeasterly at the surface to northwesterly at around 15,000 feet msl. Good thermal mixing was experience to about 6500 feet msl. Visibility ranged from five to twenty miles throughout the mission with few cumulus.


11:30
126
123
128
126
122
123
11:42
126
116
11:46
14:02
146
10 N. Mi.
(1)
144
120
116
128
133
137
126
132
11:39
83°
40°30'
146
COLUMBUS
131
131
132
132
(2)
137
12:13
137
134
154
129
136
12:05
149
156
(9)
157
146
83°
39°30'
(3)
152
146
167
132
12:20
140
144
136
12:32
132
152
133
146
(4)
152
139
151
139
151
142
12:37
12:46
167
167
(8)
149
156
(5)
159
175
149
13:02
152
177
156
149
12:51
166
182
CLINTON CO. AFB
161
(7)
189
(6)
156
156
176
13:10
157
188
179
166
13:07
DAYTON
211
168
227
171
13:25
81
13:21

FLIGHT DATE: July 16, 1974

TRUE AIRSPEED: 250.0 km/h (135 knots)

PATTERN: Square Wave

MISSION ALTITUDE: 914.4 m (3,000 ft) above msl

LOW LEVEL WINDS:	
Sfc	060°/1.54 m/s (3 knots)
609 m (2,000')	080°/5.14 m/s (10 knots)
914 m (3,000')	060°/3.60 m/s (7 knots)
1219 m (4,000')	015°/4.12 m/s (8 knots)

Low Level Winds From National Weather Service Upper Air Station Dayton, Ohio-0800 EDT

DATA: Ozone Concentration in μg/m³
Time in EDT
Hydrocarbon Sample Positions Denoted by ├────┤.

Figure C-8. Square-wave flight on July 16, 1974.

Flight Data - July 16, 1974

Square Wave

Time	Leg	O_3*	Temp. (°C)
1131	Base	126	19.4
		123	
		128	
		126	
		122	
		123	
1142	1	126	19.6
		116	
1147	2	120	19.8
		116	
		128	
		133	
		137	
		126	
		132	
1159	3	131	19.7
		132	
1205	4	136	20.0
		129	
		134	
		132	
		137	
1213	5	137	20.0
		149	
		146	
1220	6	132	20.5
		147	
		146	
		144	
		140	
		134	
1233	7	132	19.9
		139	
		142	
1237	8	152	20.4
		139	
		151	
		151	
1247	9	147	20.7
		149	
		149	
1251	10	149	20.8
		156	
		175	
		159	
		152	
1302	11	166	21.3
		161	
		156	
1308	12	157	21.0
		156	
		188	
		176	
1316	13	166	21.4
		168	
		171	
1321	14	181	21.8

- Nitrogen dioxide and nitric oxide below detectable limits.

* Concentration in μg/m^3.

Flight Data - July 16, 1974

Square-Wave (Continued)

Time	Leg	O_3*	Temp. (°C)	Time	Leg	O_3*	Temp. (°C)
1325	RETURN	227	21.0				
		211					
		189					
		189					
		182					
		177					
		156					
		147					
		139					
		146					
		152					
		152					
		157					
		154					
		154					
		151					
		146					
		144					
		146					
1403	END		20.8				

- Nitrogen dioxide and nitric oxide below detectable limits.

* Concentration in $\mu g/m^3$.

METEOROLOGICAL SUMMARY FOR FLIGHT

A generally northerly flow persisted over the Ohio area with the 3000 foot msl mission altitude winds being 06 [illegible]t 7 knots. A subsidence inversion capped the thermal mixing layer at 8800 feet msl and extended up to 11,100 feet msl with very dry air above the base of the inversion. Visibility was generally about 3 miles, but got down to one mile over Dayton.

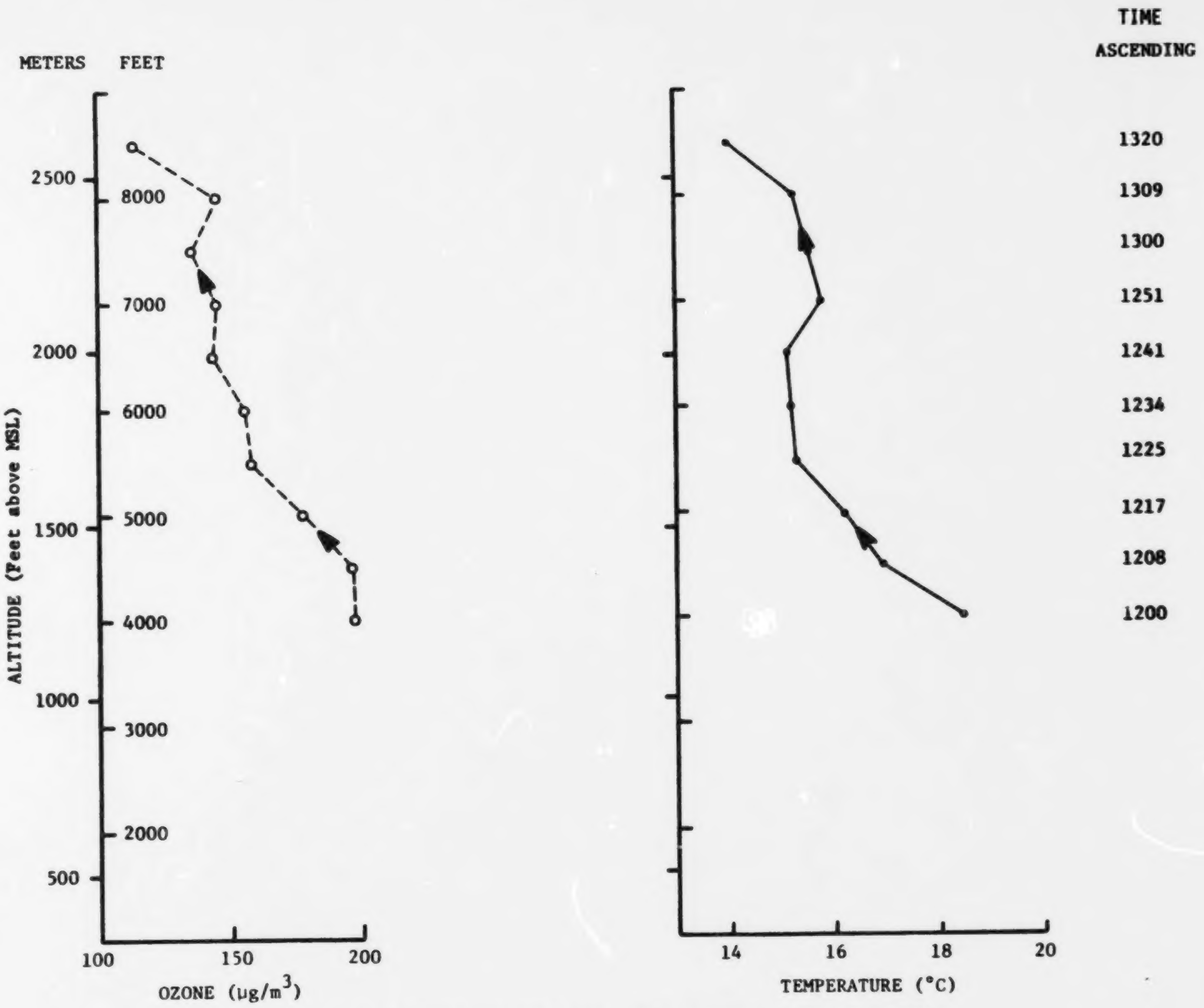


Figure C-9. Vertical profile, Wilmington; July 17, 1974.

Flight Data - July 17, 1974

Vertical Profile - Wilmington, Ohio

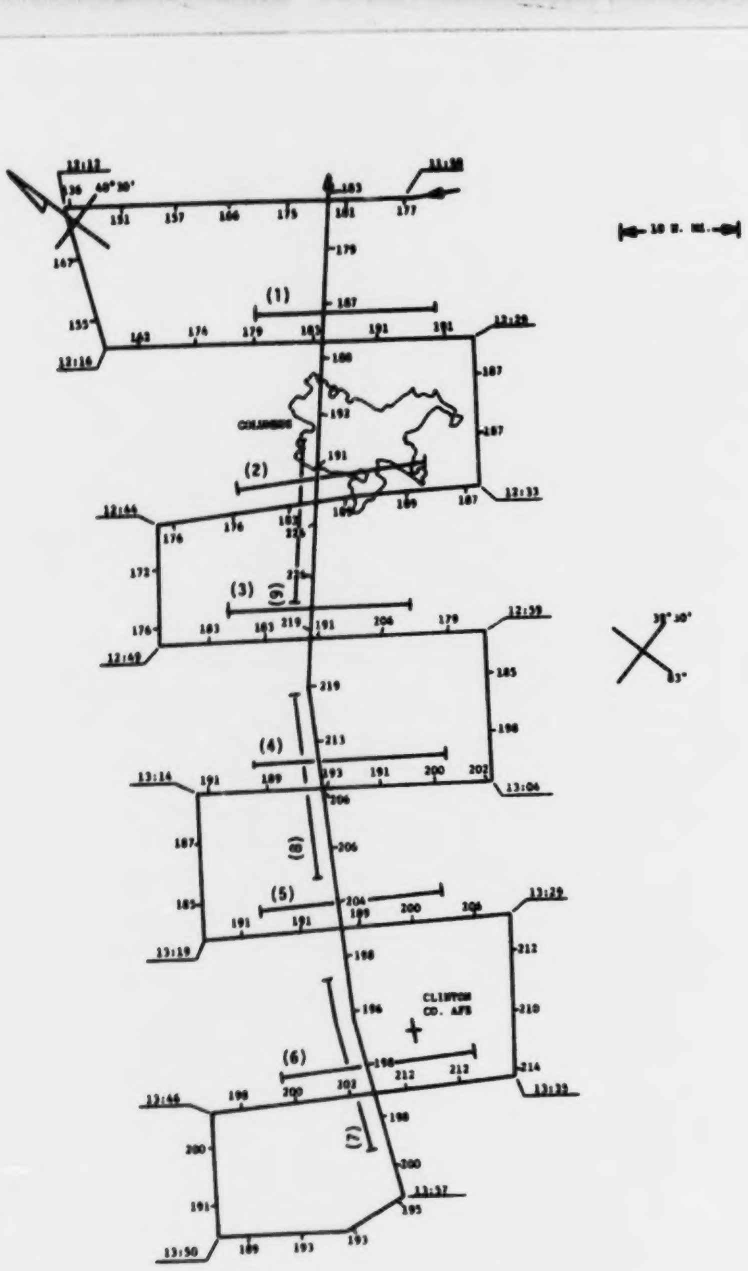
Time	Altitude (meters)	O_3*	Temp. (°C)
1155	1220	183	18.5
		204	
		203	
1203	1372	192	
		192	
		203	
1211	1525	175	16.2
		166	
		192	
1220	1678	161	15.3
		161	
		153	
1227	1830	156	15.2
		160	
		154	
1236	1983	159	15.1
		142	
		132	
1244	2135	165	15.8
		148	
		121	
		145	
1254	2288	151	15.5
		130	
		128	
1303	2440	153	15.3
		151	
		138	
		138	
1312	2593	111	14.0
		114	
		118	
		114	

- Nitrogen dioxide and nitric oxide below detectable limits.

* Concentration in $\mu g/m^3$.

METEOROLOGICAL SUMMARY FOR FLIGHT OF JULY 17, 1974

In attempting a vertical profile of a subsidence inversion, we encountered a very stable, basically isothermal layer instead between 5500 feet msl and 8800 feet msl. There was a high pressure center northeast of Pittsburgh. Winds in the stable layer were light northwesterly.


12:12
11:58
136
40°30'
183
151
157
166
175
181
177
10 N. MI.
167
179
(1)
187
155
162
174
179
183
191
191
12:29
12:16
180
187
COLUMBUS
192
187
191
(2)
12:33
12:44
176
176
183
189
189
187
226
172
226
(9)
(3)
176
183
183
219
191
206
179
12:39
39°30'
12:49
83°
219
185
213
(4)
198
13:14
191
189
193
191
200
202
13:06
206
187
206
(8)
(5)
204
13:29
185
191
191
189
200
206
13:19
212
198
CLINTON CO. AFB
196
210
(6)
198
212
212
214
13:46
198
200
202
13:33
198
(7)
200
200
191
13:57
195
13:50
189
193
193

FLIGHT DATE: July 21, 1974

PATTERN: Square Wave

TRUE AIRSPEED: 259.3 km/h (140 knots)

MISSION ALTITUDE: 975.36 m (3,200 ft) above msl

LOW LEVEL WINDS:	
Sfc	030°/3.09 m/s (6 knots)
609 m (2,000')	060°/6.17 m/s (12 knots)
914 m (3,000')	055°/4.12 m/s (8 knots)
1219 m (4,000')	025°/3.60 m/s (7 knots)

DATA: Ozone Concentration in $\mu g/m^3$
Time in EDT
Hydrocarbon Sample Positions
Denoted by ├────┤.

Low Level Winds From
National Weather Service
Upper Air Station
Dayton, Ohio-0800 EDT

Figure C-10. Square-wave flight on July 21, 1974.

Flight Data - July 21, 1974

Square Wave

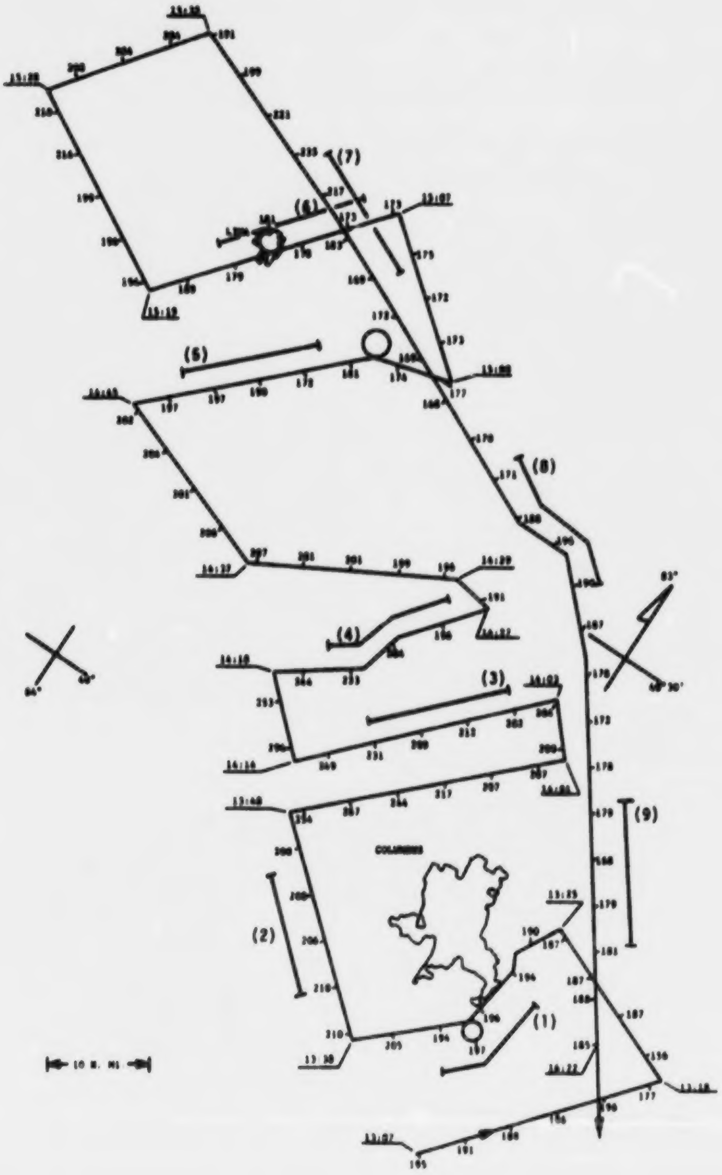
Time	Leg	O_3*	Temp. (°C)
1158	Base	177	21.8
		181	
		175	
		166	
		157	
		151	
		136	
1212	1	147	17.3
		155	
1216	2	162	18.0
		174	
		179	
		183	
		191	
		191	
1229	3	187	19.0
		187	
1234	4	187	18.5
		189	
		189	
		183	
		176	
		176	
1245	5	172	18.3
		176	
1249	6	183	18.5
		183	
		191	
		206	
		179	
1259	7	185	18.7
		198	
1304	8	202	19.0
		200	
		191	
		193	
		189	
		191	
1315	9	187	18.3
		185	
1319	10	191	18.8
		191	
		189	
		200	
		206	
1330	11	212	19.4
		210	
		214	
1335	12	212	19.8
		212	
		202	
		202	
		198	
1346	13	200	19.8
		191	
1350	14	189	19.0
		193	
		193	
		195	
1357	RETURN	200	20.5
		198	
		198	
		196	
		198	
		204	
		206	
		206	
		213	
		219	
		219	
		226	
		226	
		191	
		192	
		188	
		187	
		179	
		183	
1434	END		20.5

- Nitrogen dioxide and nitric oxide below detectable limit.

* Concentration in μg/m^3.

METEOROLOGICAL SUMMARY FOR FLIGHT OF JULY 21, 1974

An inversion aloft at 3500 feet msl was burned off by the time of the flight with thermal mixing indicated to 7600 feet msl. Winds at the 3200 foot msl flight altitude were 050° at 8 knots. Visibility ranged from 7 miles over Columbus to over 20 miles downwind of the city.


15:32
15:28
15:12
15:07
15:00
14:45
14:37
14:29
14:22
14:18
14:14
14:03
14:00
13:48
13:38
13:25
13:18
13:07
14:22
(1)
(2)
(3)
(4)
(5)
(6)
(7)
(8)
(9)
COLUMBUS
10 N. MI
84°
40°
83°
40° 30'

FLIGHT DATE: July 25, 1974

PATTERN: Square Wave

TRUE AIRSPEED: 259.3 km/h (140 knots)

MISSION ALTITUDE: 762.0 meters (2,500 ft) above msl

LOW LEVEL WINDS:	Sfc	070°/2.57 m/s (5 knots)
	609 m (2,000')	135°/3.60 m/s (7 knots)
	914 m (3,000')	130°/4.12 m/s (8 knots)
	1219 m (4,000')	110°/4.12 m/s (8 knots)

DATA: Ozone Concentration in $\mu g/m^3$
Time in EDT

Hydrocarbon Sample Positions
Denoted by ├────────┤ .

Low Level Winds From
National Weather Service
Upper Air Station
Dayton, Ohio-0800 EDT

Figure C-11. Square-wave flight on July 25, 1974.

Flight Data - July 25, 1974

Square Wave

Time	Leg	O_3*	Temp. (°C)	Time	Leg	O_3*	Temp. (°C)
1308	Base	195	21.5	1418	8	244	
		191				233	
		188				204	
		186				196	22.5
		196					
		177	22.0	1427	9	191	22.5
1318	1	156	22.0	1429	10	196	
		187				199	
		187	21.5			201	
		187				201	
						207	23.0
1327	2	190	22.5				
		194		1438	11	206	23.0
		196				201	22.3
		197				204	22.5
		194				202	23.0
		205	22.7				
				1446	12	197	23.0
1338	3	210	22.7			197	
		210				197	23.1
		206	22.5			172	
		208				181	22.5
		208				174	
						177	22.5
1348	4	254	22.0				
		267		1500	13	175	
		244				172	22.5
		217	22.5			173	
		207					
		207		1507	14	173	22.5
						173	
1401	5	200	22.5			178	
		204				181	23.0
						179	
1403	6	202	23.0			189	22.0
		212					
		209		1519	15	194	22.0
		231				196	
		249	23.0			199	22.2
						216	
1414	7	296	23.0			210	23.5
		253					

- Nitrogen dioxide and nitric oxide below detectable limit.

* Concentration in $\mu g/m^3$.

Flight Data - July 25, 1974

Square Wave (Continued)

Time	Leg	O_3*	Temp. (°C)	Time	Leg	O_3*	Temp. (°C)
1528	16	208	23.5	1536 (Cont'd)	17	188	23.0
		204	22.4			196	
		204	23.0			190	
						187	22.0
1536	17 (return by Pattern)	191				178	
		199				172	21.0
		221				178	20.0
		235	23.9			179	
		217				168	22.0
		183				179	24.0
		169				181	
		172				188	
		169	24.9				
		168		1622		185	25.0
		170					
		171					

- Nitrogen dioxide and nitric oxide below detectable limit.

* Concentration in μg/m^3.

METEOROLOGICAL SUMMARY FOR FLIGHT

On this day, the Ohio Valley was between fronts with generally easterly flow near the surface. Visibility ranged from 2 to 5 miles with moderate turbulence. Thermal mixing occurred to 7000 feet msl with cumulus forming at 3500 feet msl.

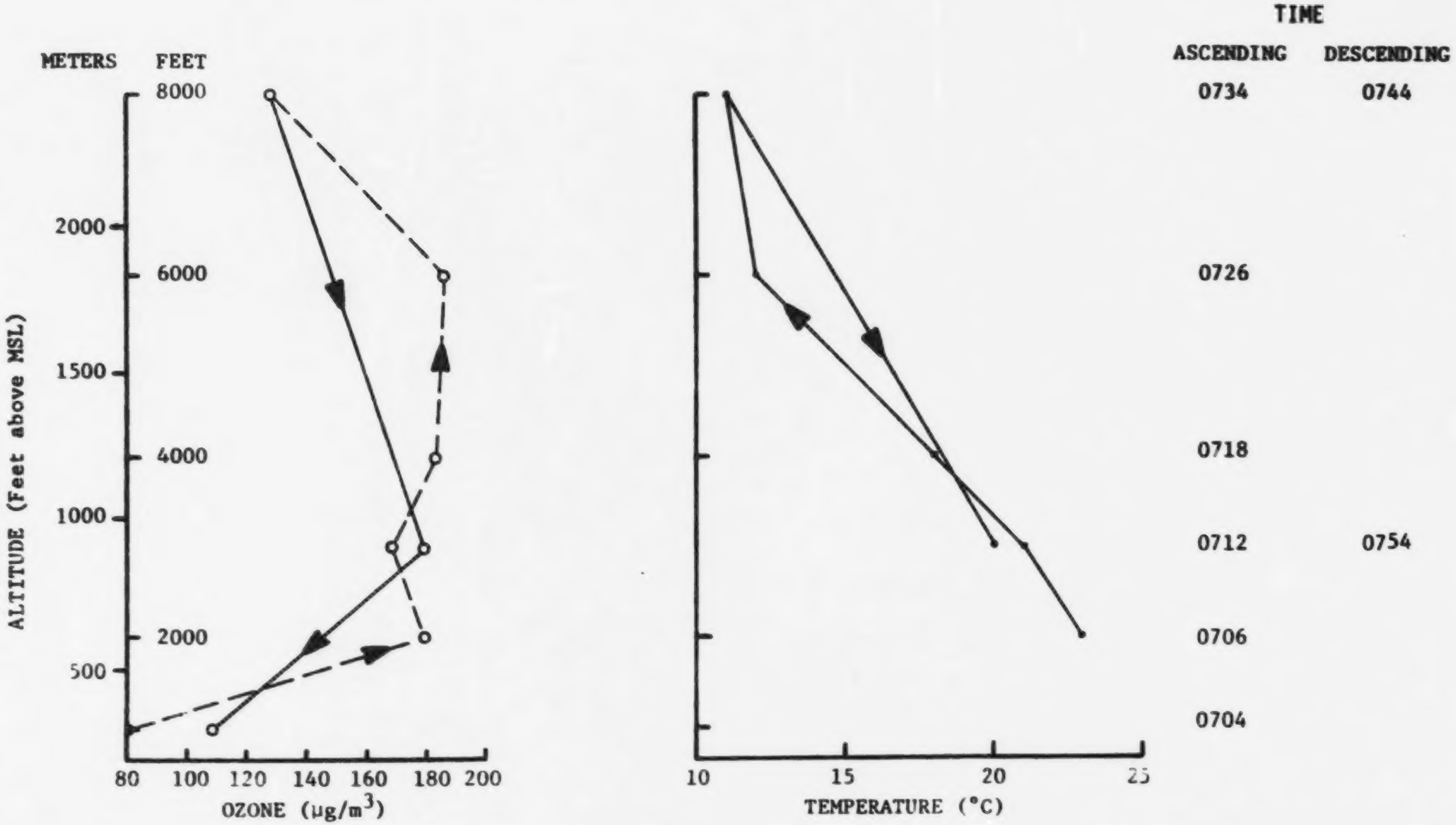


Figure C-12. Vertical profile, Wilmington; August 1, 1974.

Flight Data - August 1, 1974

Vertical Profile - Wilmington, Ohio

Time	Altitude (meters)	O_3*	Temp. (°C)
0704	305	80	
0706	610	179	23
0712	915	168	21
0718	1220	183	18
0726	1830	186	12
0744	2440	128	11
0803	915	179	20
0810	Low Pass	109	

- Nitrogen dioxide and nitric oxide below detectable limits.

* Concentration in $\mu g/m^3$.

METEOROLOGICAL SUMMARY FOR FLIGHT

High pressure centered over eastern West Virginia produced southwesterly flow through Ohio. By afternoon, good thermal mixing was experienced to the base of a shallow inversion between 8200 feet msl and 9000 feet msl. By 1900, the inversion had burned off.

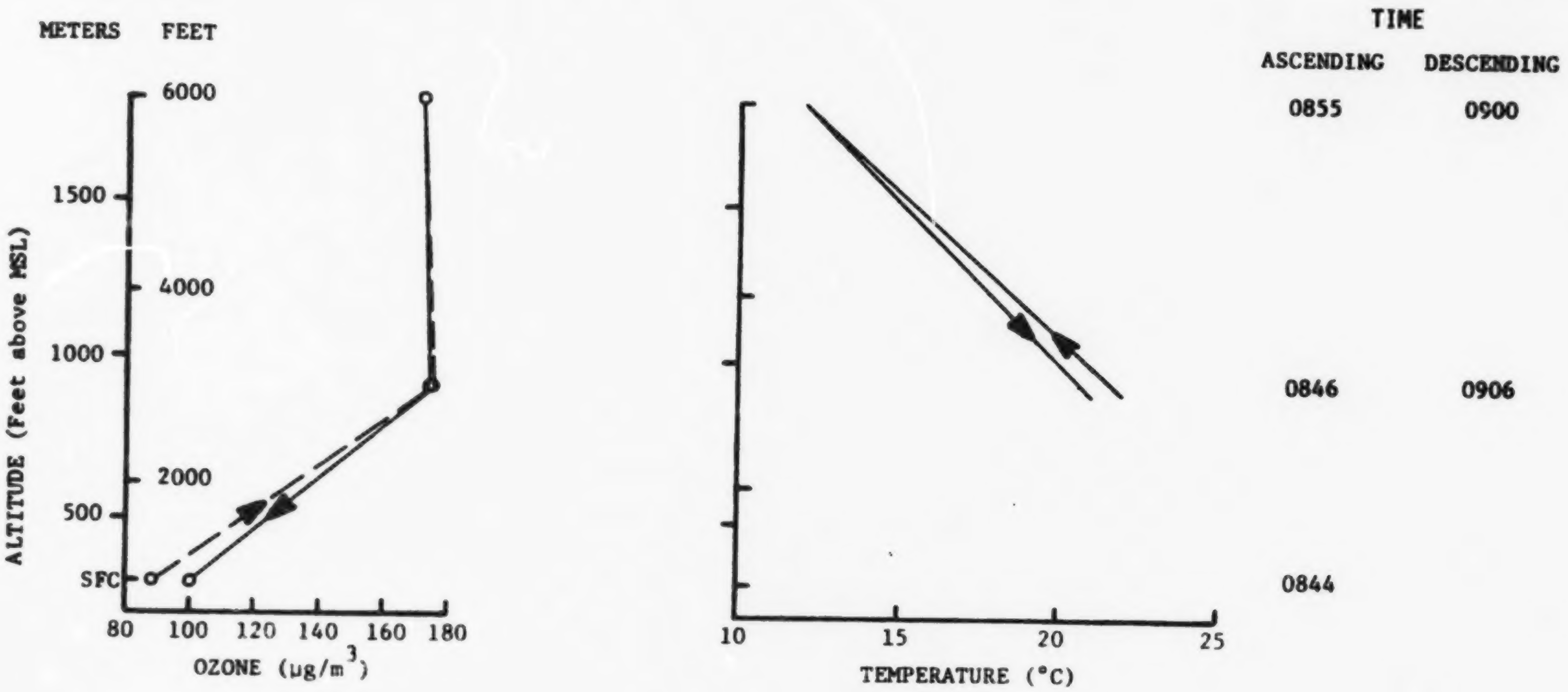


Figure C-13. Vertical profiles, Wilmington, August 1, 1974.

Flight Data - August 1, 1974

Vertical Profile - Wilmington, Ohio

Time	Altitude (meters)	O_3*	Temp. (°C)
0844	Low Pass	88	
0850	915	175	22
0900	1830	171	12
0910	919	174	21
0913	Low Pass	100	

- Nitrogen dioxide and nitric oxide below detectable limits.

* Concentration in $\mu g/m^3$.

METEOROLOGICAL SUMMARY FOR FLIGHT

High pressure centered over eastern West Virginia produced southwesterly flow through Ohio. By afternoon, good thermal mixing was experienced to the base of a shallow inversion between 8200 feet msl and 9000 feet msl. By 1900, the inversion had burned off.

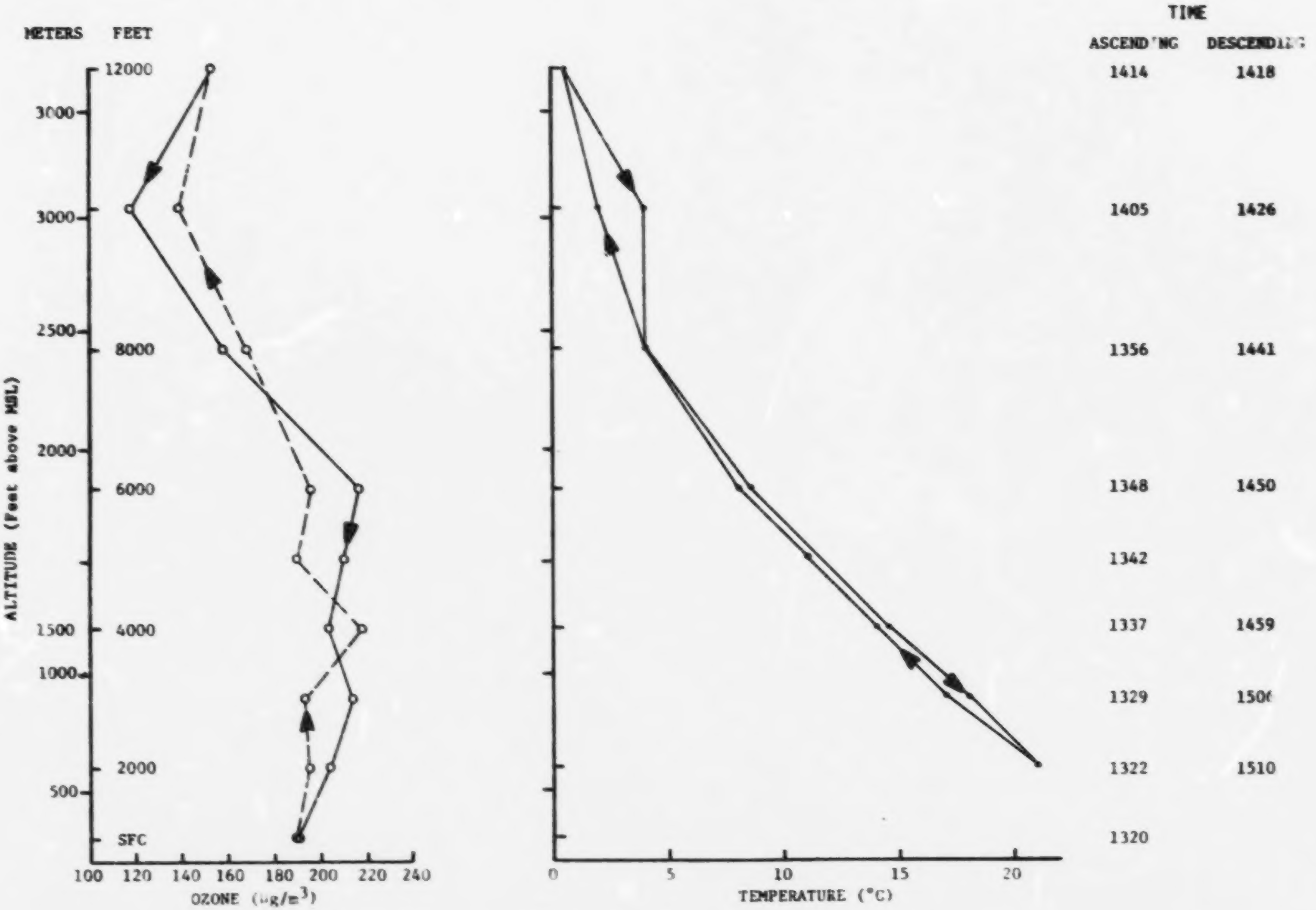


Figure C-14. Vertical profile, Wilmington; August 1, 1974.

Flight Data - August 1, 1974

Time	Altitude (meters)	O_3*	Temp. (°C)
1320	Low Pass	189	
1327	610	195	26
1335	915	193	22
1340	1220	218	19
1346	1525	189	16
1352	1830	196	13
1402	2440	158	9
1410	3050	139	7
1418	3660	153	
1432	3050	118	9
1446	2440	158	9
1455	1830	217	13.5
1502	1220	208	19.5
1508	915	214	23
1515	610	204	26
1516	Low Pass	190	

- Nitrogen dioxide and nitric oxide below detectable limits.

* Concentration in $\mu g/m^3$.

METEOROLOGICAL SUMMARY FOR FLIGHT

High pressure centered over eastern West Virginia produced southwesterly flow through Ohio. By afternoon, good thermal mixing was experienced to the base of a shallow inversion between 8200 feet msl and 9000 feet msl. By 1900, the inversion had burned off.

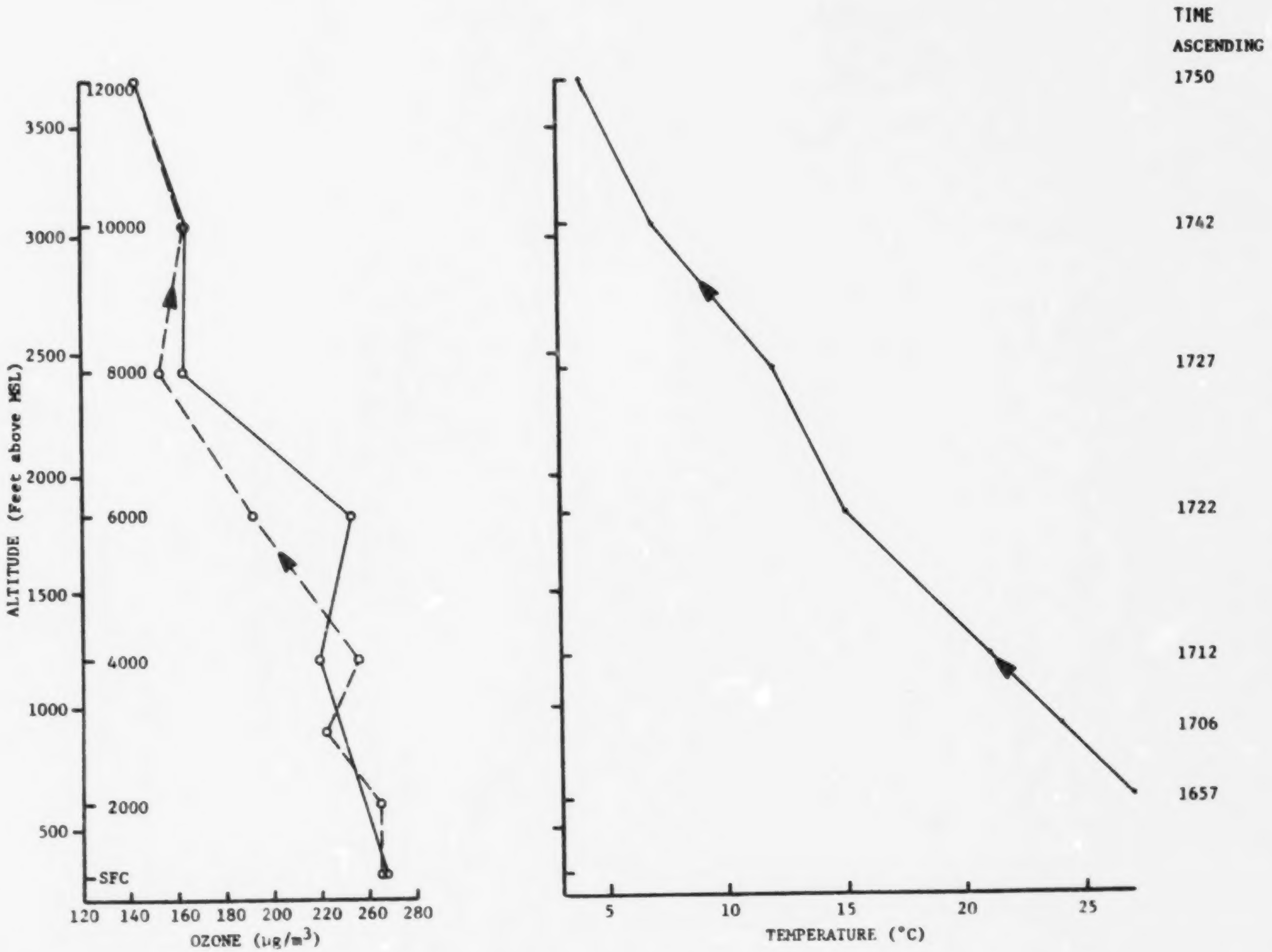


Figure C-15. Vertical profile, Wilmington; August 1, 1974.

Flight Data - August 1, 1974

Vertical Profile - Wilmington, Ohio

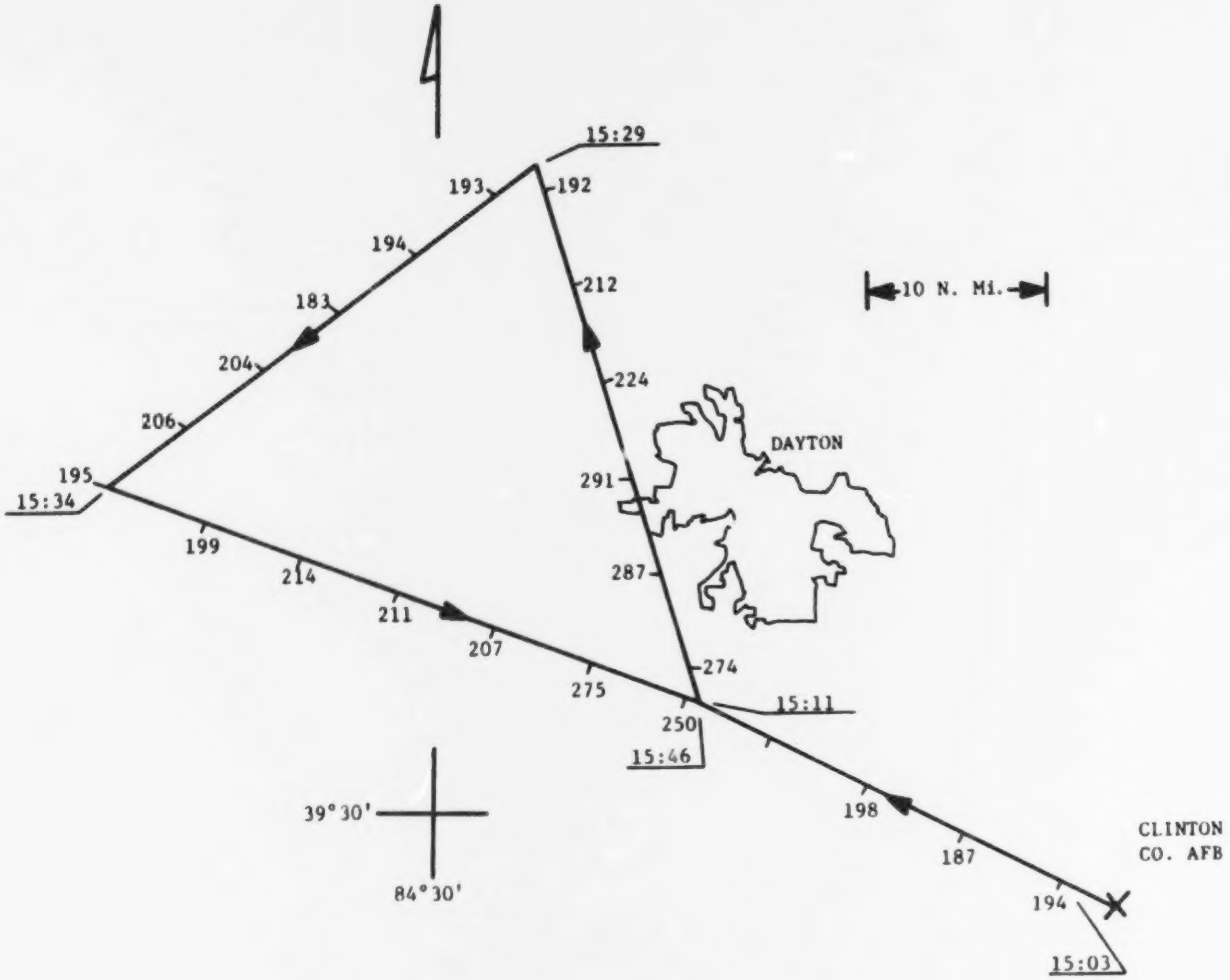
Time	Altitude (meters)	O_3*	Temp. (°C)
1656	Low Pass	245	
1705	610	245	27
1710	915	222	24
1718	1220	236	21
1724	1830	192	15
1739	2450	153	12
1746	3050	164	7
1753	3630	143	4
1758	3050	165	
1802	2450	163	
1805	1830	233	
1812	1220	219	18.8
1816	Low Pass	247	

- Nitrogen dioxide and nitric oxide below detectable limits.

* Concentration in $\mu g/m^3$.

METEOROLOGICAL SUMMARY FOR FLIGHT

High pressure centered over eastern West Virginia produced sourthwesterly flow through Ohio. By afternoon, good thermal mixing was experienced to the base of a shallow inversion between 8200 feet msl and 9000 feet msl. By 1900, the inversion had burned off.


15:29
193
192
194
212
183
10 N. Mi.
204
224
206
DAYTON
195
15:34
291
199
287
214
211
207
274
275
15:11
250
15:46
198
39°30'
CLINTON
CO. AFB
187
84°30'
194
15:03

FLIGHT DATE: August 9, 1974

PATTERN: EPA-RTI/Batelle Comparison Flight

TRUE AIRSPEED: 240.8 km/h (130 knots)

MISSION ALTITUDE: 609.6 m (2,000 ft) above msl

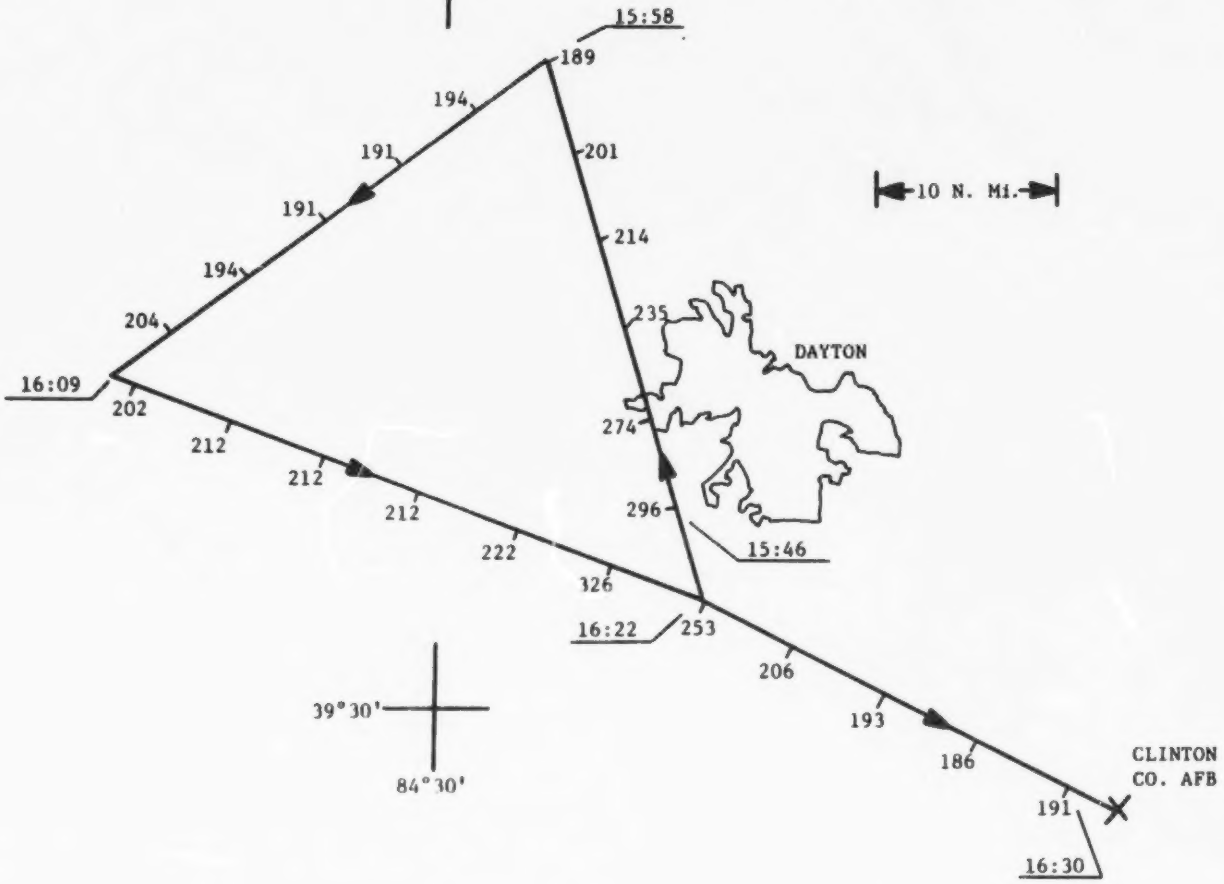
LOW LEVEL WINDS: Sfc 220°/2.06 m/s (4 knots)
609 m (2,000') 285°/3.60 m/s (7 knots)
914 m (3,000') 295°/3.09 m/s (6 knots)
1219 m (4,000') 295°/2.57 m/s (5 knots)

DATA: Ozone Concentration in ug/m^3
Time in EDT

Low Level Winds From National Weather Service Upper Air Station, Dayton, Ohio-0800 EDT

Figure C-16a. EPA-RTI/Battelle comparison flight on August 9, 1974.

4


15:58
189
194
191
191
194
204
16:09
202
212
212
212
222
326
16:22
253
201
214
235
274
296
15:46
DAYTON
10 N. Mi.
206
193
186
191
16:30
CLINTON
CO. AFB
39°30'
84°30'

FLIGHT DATE: August 9, 1974

PATTERN: EPA-RTI/Batelle Comparison Flight

TRUE AIRSPEED: 240.8 km/h (130 knots)

MISSION ALTITUDE: 609.6 m (2,000 ft) above msl

LOW LEVEL WINDS:	
Sfc	220°/2.06 m/s (4 knots)
609 m (2,000')	285°/3.60 m/s (7 knots)
914 m (3,000')	295°/3.09 m/s (6 knots)
1219 m (4,000')	295°/2.57 m/s (5 knots)

DATA: Ozone Concentration in ug/m^3
Time in EDT

Low Level Winds From National Weather Service Upper Air Station, Dayton, Ohio-0800 EDT

Figure C-16b. EPA-RTI/Battelle comparison flight on August 9, 1974.

Flight Data - August 9, 1974

EPA-RTI/Batelle Comparison Flight

Time	Leg	O_3*	Temp. (°C)
1503	Wilmington to Montgomery County	194	27
		187	
		198	
		off scale	
1511	Montgomery County to Dayton	274	27
		287	
		241	
		224	
		212	
		192	
1529	Dayton to Richmond	193	27
		194	
		193	
		204	
		206	
		195	
1534	Richmond to Montgomery County	199	27
		214	
		211	
		207	
		275	
	(over Montgomery Co.)	250	26
1546	Montgomery County to Dayton	296	27
		274	
		235	
		214	
		201	
	(over Dayton)	189	

- Nitrogen dioxide and nitric oxide below detectable limits.

[*] Concentration in $\mu g/m^3$.

Flight Data - August 9, 1974

EPA-RTI/Batelle Comparison Flight (Continued)

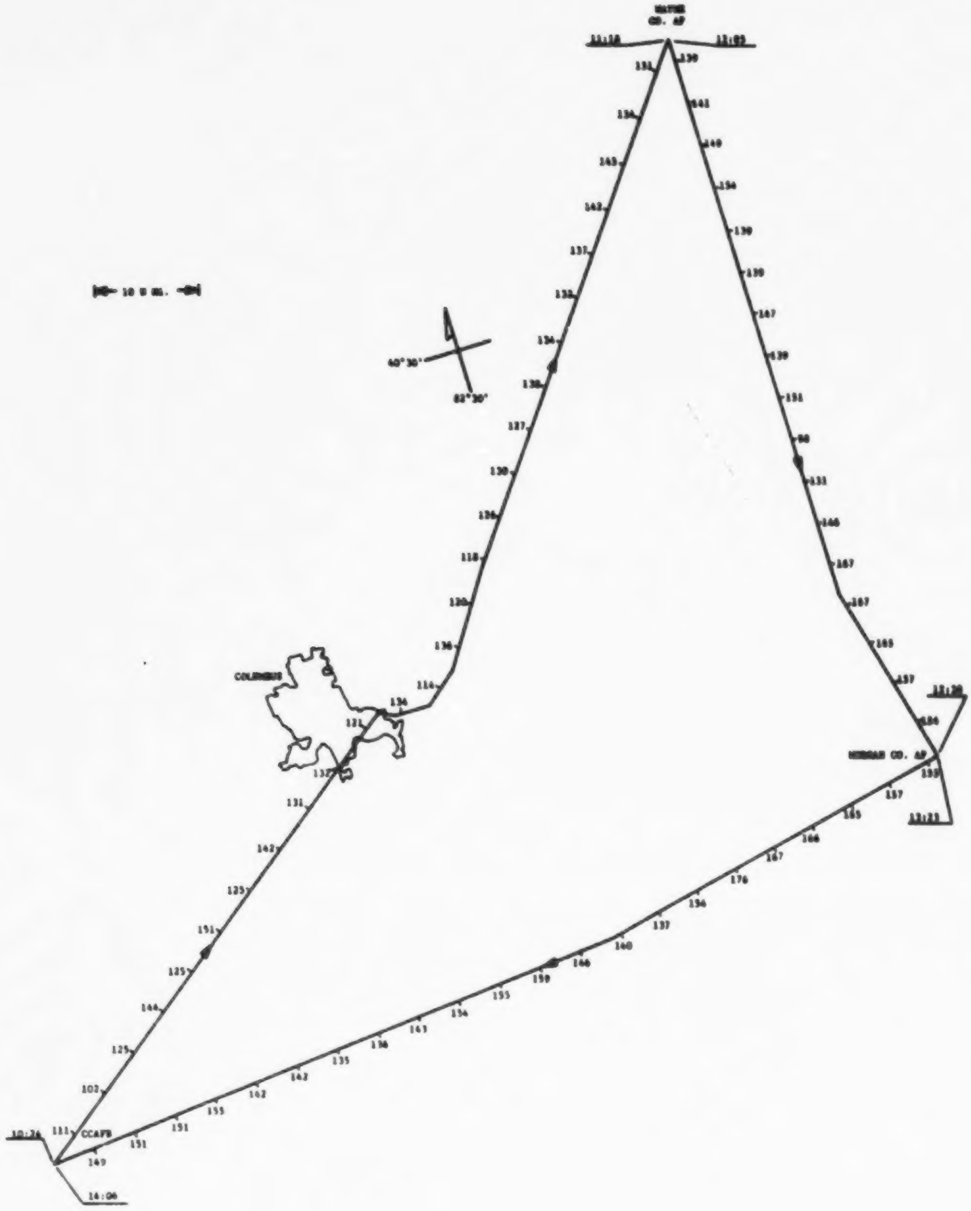
Time	Leg	O_3*	Temp. (°C)
1558	Dayton to Richmond	194	27
		191	
		191	
		194	
		204	
1609	Richmond to Montgomery County	202	27
		212	
		212	
		212	26
		222	
		326	
1622	(over Montgomery Co.)	253	26
	Montgomery County to Wilmington	206	
		193	
		186	
		191	
1634	Low Pass	187	
1640	Wilmington	141	

- Nitrogen dioxide and nitric oxide below detectable limits.

* Concentration in μg/m^3.

METEOROLOGICAL SUMMARY FOR FLIGHT

There was a dissipating cold front north of the Dayton area. Surface winds were light and generally easterly at the time of the mission. Visibility was around 7 miles.


CO. AP
11:18
12:03
131
130
136
141
143
140
142
136
131
130
132
130
134
167
130
139
127
151
130
90
126
131
118
146
120
167
136
167
116
185
COLUMBUS
137
134
12:26
121
134
CO. AP
132
132
131
157
12:23
142
165
166
125
167
176
151
136
125
137
160
144
166
159
125
155
134
102
161
136
135
10:26
142
111
CCAFB
142
155
151
151
149
14:06
10 n mi.
40°30'
82°30'

FLIGHT DATE: August 13, 1974

TRUE AIRSPEED: 250.0 km/h (135 knots)

LOW LEVEL WINDS: Sfc

609 m (2,000')

914 m (3,000')

1219 m (4,000')

DATA: Ozone Concentration in μg/m^3
Time in EDT

PATTERN: Ohio Ground Station Interlock

MISSION ALTITUDE: 762.0 m (2,500 ft) above msl

205°/2.57 m/s (5 knots)

255°/8.74 m/s (17 knots)

270°/8.74 m/s (17 knots)

270°/8.23 m/s (16 knots)

Low Level Winds From National Weather Service
Upper Air Station, Dayton, Ohio-0800 EDT

Figure C-17a. Ohio ground station interlock flight on August 13, 1974.

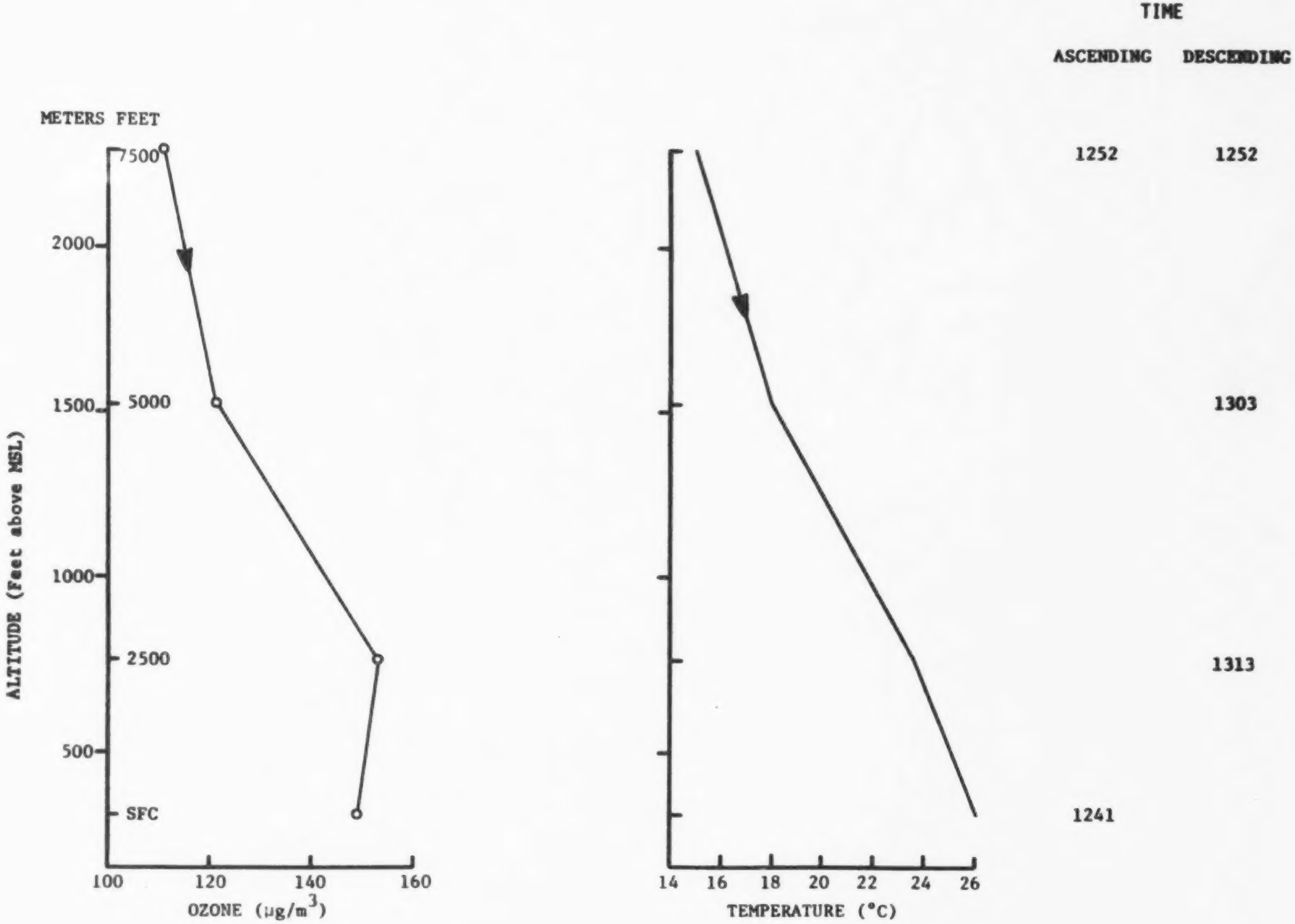


Figure C-17b. Vertical profile, McConnelsville; August 13, 1974.

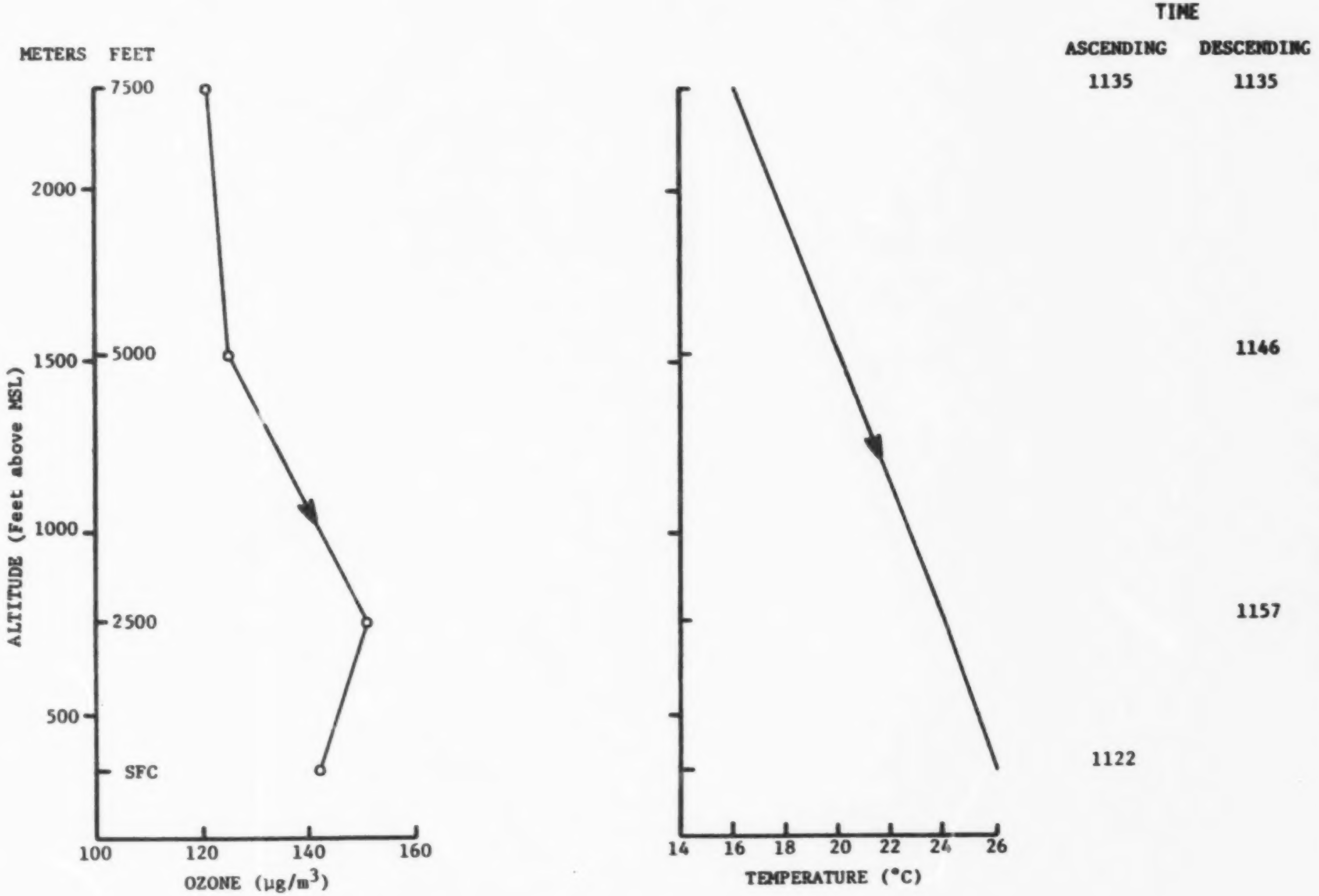


Figure C-17c. Vertical profile, Wooster; August 13, 1974.

Flight Data - August 13, 1974

Vertical Profile - Wooster and McConnelsville

Time	Event	O_3*	Temp. (°C)
1025	Wilmington to Wooster	111	23
	(792 meters)	102	
		125	
		144	
		125	
		151	
		125	
		142	
		131	
		132	
		121	
		134	
		114	
		136	23.7
		120	
		118	
		126	
		130	
		127	
		130	
		134	
		132	
		137	
		142	
		145	
1117		134	
Vertical Profile at Wooster			
1122	Low Pass	142	26.4
	2288 meters	122	15.4
	1525 meters	125	21
	752 meters	152	25
1206	Wooster to McConnelsville	141	
	(792 meters)	149	
		154	
		139	
		139	
		147	
		139	
		131	
		98	

- Nitrogen dioxide and nitric oxide below detectable limits.

* Concentration in $\mu g/m^3$.

Flight Data - August 13, 1974

Vertical Profile - Wooster and McConnelsville (Continued)

Time	Event	O_3*	Temp. (°C)
1206	Wooster to McConnelsville	131	
	(792 meters)	146	23.8
	(Continued)	167	
		167	
		165	
		157	
1238		154	
Vertical Profile at McConnelsville			
1141	Low Pass		26.3
1157	(2288 meters)	117	14.5
1206	(1525 meters)	120	19.2
1219	(762 meters)	136	24.4
1223	McConnelsville to Wilmington	155	
	(762 meters)	157	
		165	
		166	
		167	
		176	
		154	
		137	
		140	
		146	
		159	
		155	
		154	
		143	
		136	
		135	
		142	
		142	
		155	
		151	
		151	
1306		149	25.6

- Nitrogen dioxide and nitric oxide below detectable limits.

* Concentration in μg/m^3.

METEOROLOGICAL SUMMARY FOR FLIGHT OF AUGUST 13, 1974

High pressure over West Virginia produced generally westerly low level flow over Ohio. There was a high overcast with relatively good visibility and thermal mixing through a fairly shallow layer to 4000 feet msl.

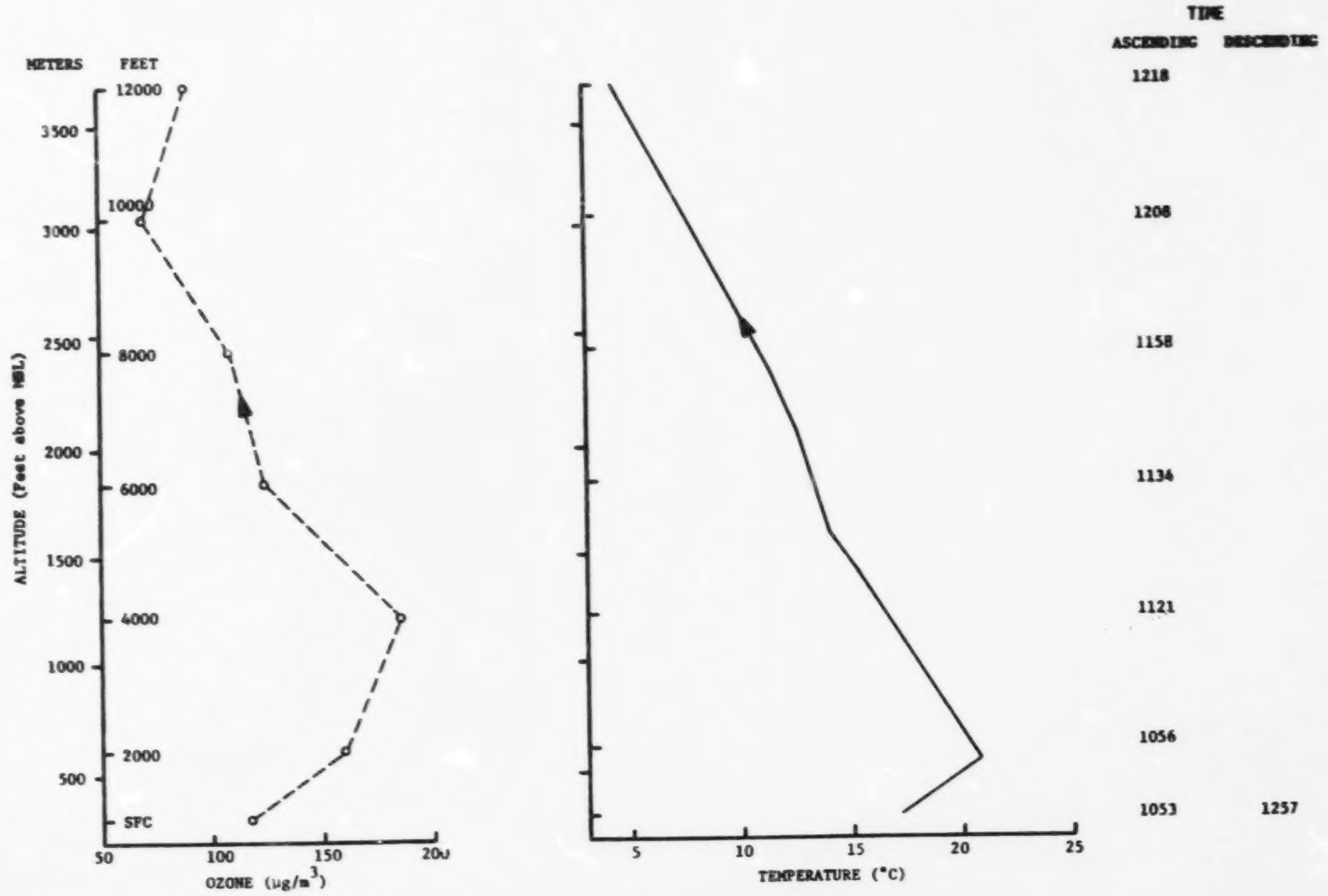


Figure C-18. Vertical profile, Wilmington; August 15, 1974.

Flight Data - August 15, 1974

Vertical Profile - Wilmington

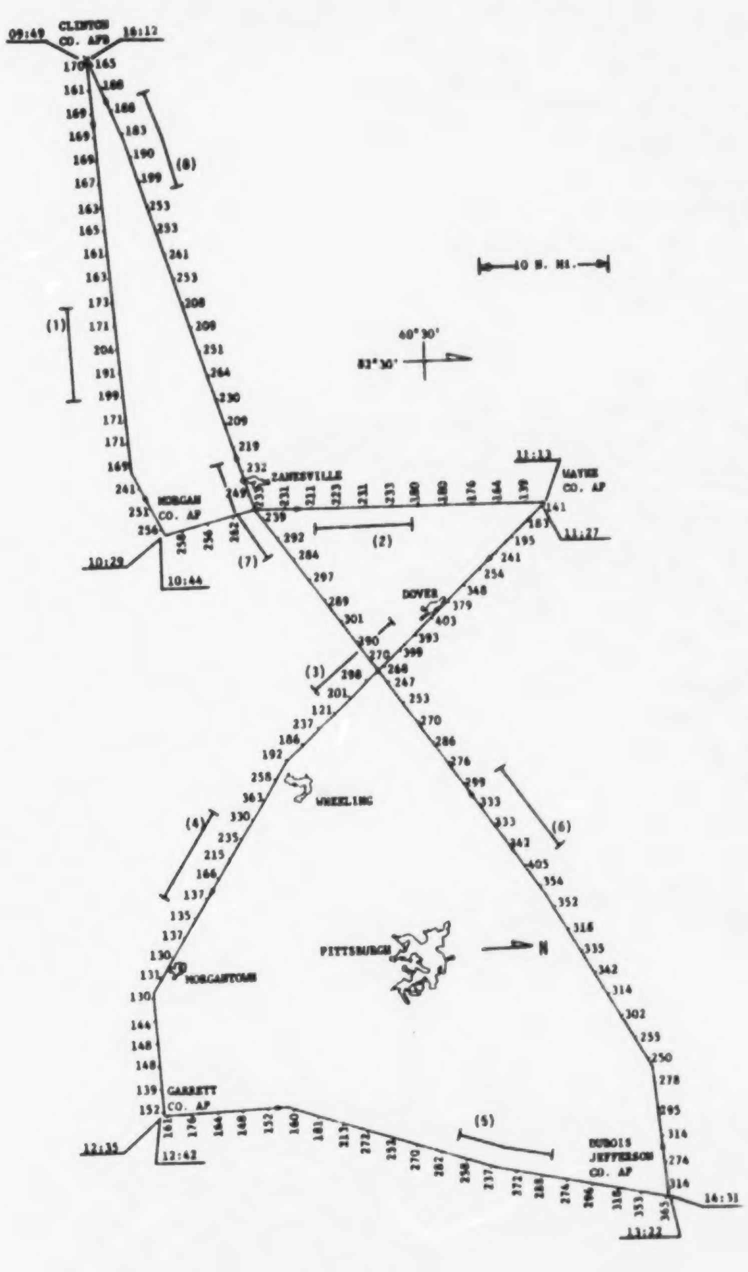
Time	Altitude (meters)	O_3^*
1053	Low Pass	117
1117	610	160
1130	1220	186
1153	1830	124
1201	2440	109
1215	3050	70
1228	3660	90

- Nitrogen dioxide and nitric oxide below detectable limits.

* Concentration in $\mu g/m^3$.

METEOROLOGICAL SUMMARY FOR FLIGHT

Ohio was experiencing a light northerly flow. Good thermal mixing occurred to 7500 feet msl with visibility about 5 miles due to haze. Few cumulus formed at 4000 feet msl.


CLINTON CO. AFB
09:49
16:12
10 N. MI.
40°30'
82°30'
(1)
(2)
(3)
(4)
(5)
(6)
(7)
(8)
ZANESVILLE
MORGAN CO. AP
10:29
10:44
WAYNE CO. AP
11:13
11:27
DOVER
WHEELING
PITTSBURGH
N
MORGANTOWN
GARRETT CO. AP
12:35
12:42
DUBOIS JEFFERSON CO. AP
14:31
13:22

FLIGHT DATE: August 21, 1974

PATTERN: Eastern Stagnation Ground Station Interlock

TRUE AIRSPEED: 250 km/h (135 knots)

MISSION ALTITUDE: 1219 m (4000 ft) above msl

LOW LEVEL WINDS: Sfc 140°/2.06 m/s (4 knots)

609 m (2,000') 145°/5.66 m/s (11 knots)

914 m (3,000') 130°/6.69 m/s (13 knots)

1219 m (4,000') 140°/6.69 m/s (13 knots)

DATA: Ozone Concentration in $\mu g/m^3$
Time in EDT

Hydrocarbon Sample Positions
Denoted by |———| .

Low Level Winds From
National Weather Service
Upper Air Station
Dayton, Ohio-0800 EDT

Figure C-19. Eastern flight of August 21, 1974.

Flight Data - August 21, 1974

Time	Event	O_3*	Temp.
0949	Wilmington to McConnelsville (1220 meters)	170	20.7
		161	
		169	
		169	
		167	
		163	19.8
		165	
		161	
		163	
		173	
		171	
		204	
		191	
		199	
		171	19.7
		171	
		169	20.3
		241	
		251	
1029		256	20.2
1044	McConnelsville to Wooster (1220 meters)	258	20.3
		256	20.0
		262	
		233	
		231	20.5
		223	
		231	
		233	
		180	20.0
		180	
		176	
		164	20.6
1113		139	19.9
1127	Wooster to Garrett Co.	141	20.5
		183	
		195	
		241	
		254	
		348	
		379	
		403	
		393	
		399	
		268	
1150	Wooster to Garrett Co. (Cont'd)	298	19.5
		201	
		121	
		237	
		186	
		192	
		258	
		363	20.7
		330	
		235	
		215	
		166	19.9
		137	
		135	
		137	
		130	
		131	20.4
		130	
		144	
		148	
		148	
		139	
1235		152	18.9
1242	Garrett Co. to DuBois	161	19.6
		176	19.0
		164	
		148	
		152	
		160	
		181	
		213	
		272	
		252	
		270	21.0
		282	
		258	
		237	
		272	
		288	
		274	
		296	
		318	20.9
		353	
1322		365	21.3

- Nitrogen dioxide and nitric oxide below detectable limits.

* Concentration in $\mu g/m^3$.

Flight Data - August 21, 1974 (Continued)

Time	Event	O_3*	Temp. (°C)	Time	Event	O_3*	Temp. (°C)
1431	DuBois to Wilmington	314	22.1	(1431)	DuBois to Wilmington (Cont'd)	290	
		274				301	
		314				289	
		295				297	
		278				284	
		250				292	
		255				239	
		302				249	
		314				232	
		342				219	
		335	21.1			209	
		318				230	
		352				264	
		354				251	
		405				209	
		342	21.7			208	
		333				253	
		333				241	
		299				253	
		276				253	21.2
		286				199	
		270				190	
		253	20.9			183	
		247				188	
		270				188	

- Nitrogen dioxide and nitric oxide below detectable limits.

* Concentration in μg/m^3.

METEOROLOGICAL SUMMARY FOR FLIGHT

A high pressure center had been moving steadily eastward through the mission area for three days and was now centered over southern New England. However, relatively high pressure, light surface winds and poor visibility still prevailed in our area of operations. Flow was generally from the southeast. A shallow subsidence inversion at 12,000 feet msl was not penetrated during the mission which was flown at 4000 feet msl. Thermal mixing was through a deep layer to 9500 feet msl. A layer of altocumulus covered the southern half of the mission area from Wilmington to Garrett County during the morning but had either moved south or dissipated by late afternoon. There was a field of building cumulus over western Pennsylvania during the afternoon with bases around 6000 feet msl. Visibility varied throughout the mission ranging from as little as 2 miles to as much as 20 miles.

APPENDIX D

OZONE AND OXIDES OF NITROGEN ANALYZER EVALUATION AT REDUCED PRESSURE

D-1 Introduction and Summary

A series of tests were conducted in an altitude chamber at the National Environmental Research Center at Las Vegas, Nevada. The purpose of these tests was to determine the characteristic behavior of a Bendix NO-NO_2-NO_x analyzer, a Bendix O_3 analyzer, and an RTI solid phase chemiluminescent O_3 meter to changing altitude, as in unpressurized aircraft. Two of these instruments were subsequently used in the aircraft measurement program for the Summer 1974 Oxidant Study.

The instruments were placed in the chamber and calibrated at ambient pressure. The chamber was then sealed and partially evacuated simulating a higher altitude environment. Calibration gases were generated externally from a calibration system operating at a constant ambient pressure, and drawn into the chamber to the gas analyzer inputs, to insure constant calibration levels with changing pressure. Tests were run over the range of pressures corresponding to ground level to an altitude of approximately 5,000 meters (18,000 feet). Test results demonstrated that all instruments responded in a repeatable manner to variations in pressure. Typically the output of the instrument dropped nearly in proportion to the density of the air sample. From these data, graphs were constructed whereby a single correction factor could be determined for each instrument at an altitude. The effects of altitude on the instrument then could be compensated for by multiplying by that correction factor.

To insure that the results of these tests were applicable over an extended period of time to the specific instruments tested, checks were made on instruments during flight. Flow rate checks were made periodically on the instruments to insure that the flow dynamics of the instruments did not change with time, for this would affect the behavior of the instrument with varying altitude. Also, as a check, in-flight calibrations were performed twice on the instruments during the 3-month project. Results of these showed the same response for varying pressure as was determined during the chamber tests. However, more critical logistical problems existed in the aircraft for these tests making them significantly more difficult to perform accurately in the air than in a test chamber (for example, the problem

Preceding page blank

of producing known ozone concentration while the ozone generator pressure varies and the problem of carrying extra gas cylinders in an aircraft already loaded to capacity).

D-2 Test Set-up

The O_3 and NO-NO_2-NO_x analyzers were mounted inside a Weber Pressure Chamber, Model WF-27-40 + 200 HV. A schematic diagram of the chamber is shown in figure D-1, illustrating the chamber controls, support gases and signal lines to the analyzers and the sample manifold system. The glass sample manifold was mounted inside the chamber, with the downstream end exhausted into the chamber. Teflon tubing was used to connect the sample inlet of each instrument to the manifold. Oxygen and ethylene gases were conveyed to the instruments inside the chamber, through .318 cm i.d. s.s. tubing passed through .635 cm o.d. bulkhead Swagelok connectors. The s.s. tube to Swagelok fitting seal was completed with a 2.54 cm o.d. sleeve of .318 cm i.d., .635 cm o.d. Teflon tube as shown in figure D-2. The ethylene exhausted from the ozone analyzer was vented into the chamber after being passed through a catalytic converter.

A descriptive diagram of the calibration system is shown in figure D-3. The apparatus consists of a clean air source, compressed cylinder of nitric oxide in nitrogen, regulating valves, flow meters, an ozone generator, and mixing flasks.

D-3 Calibration Gases

Ozone concentrations in $\mu g/m^3$ for various ozone generator sleeve settings were determined using the Neutral-Buffered Potassium Iodide Method described in the April 30, 1971 Edition of the Federal Register.

Nitric oxide span concentrations were obtained by diluting pressurized NO in nitrogen with zero air. Nitrogen dioxide span concentrations were generated by the gas phase titration technique, where the gas phase reaction between NO and O_3 was assumed to produce a stochiometric quantity of NO_2:

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad (1)$$

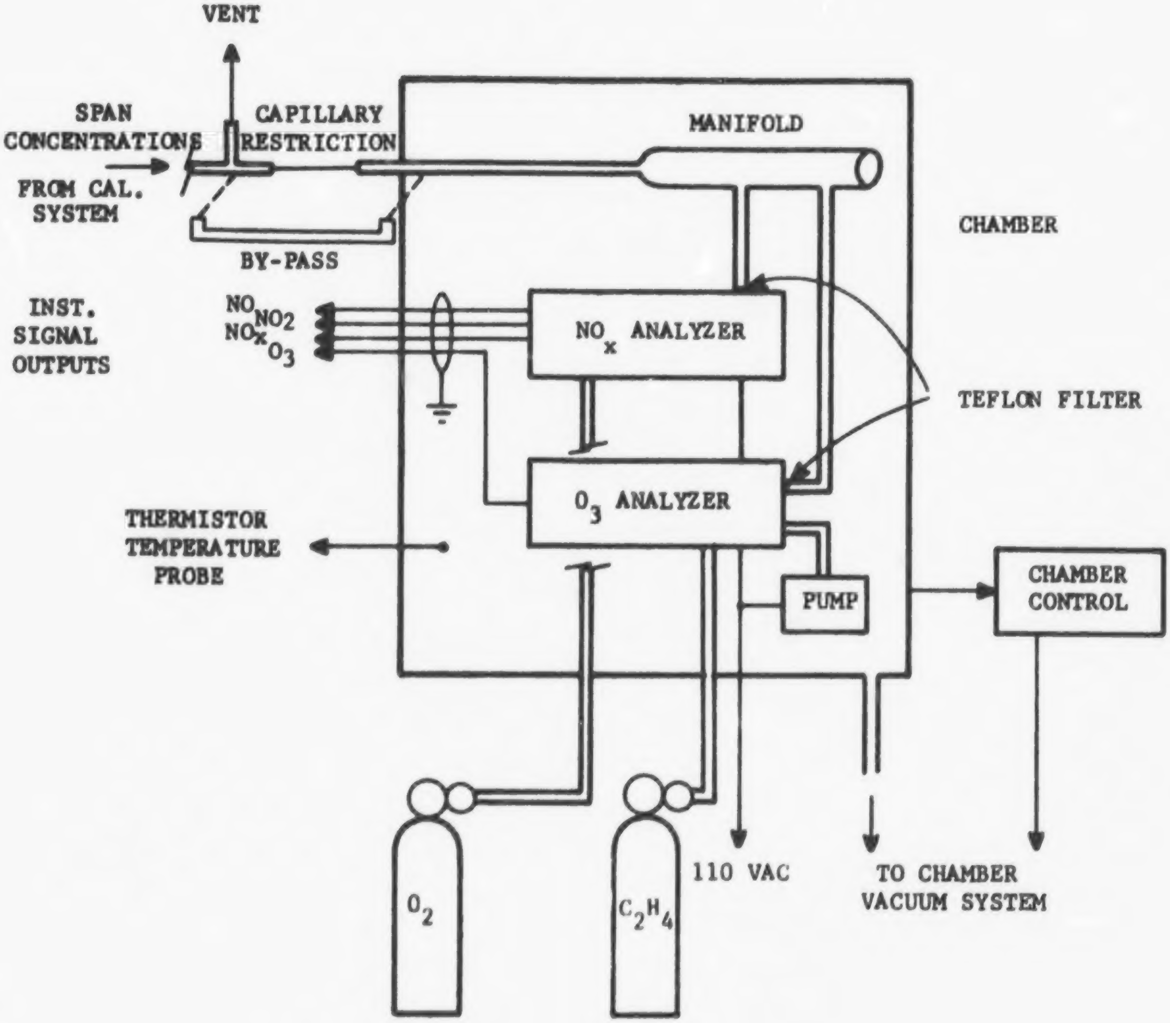

VENT
SPAN CONCENTRATIONS FROM CAL. SYSTEM
CAPILLARY RESTRICTION
MANIFOLD
CHAMBER
BY-PASS
INST. SIGNAL OUTPUTS
NO
NO2
NOx
O3
NOx ANALYZER
TEFLON FILTER
O3 ANALYZER
THERMISTOR TEMPERATURE PROBE
PUMP
CHAMBER CONTROL
110 VAC
TO CHAMBER VACUUM SYSTEM
O2
C2H4

Figure D-1. Schematic diagram of test set-up in pressure chamber.

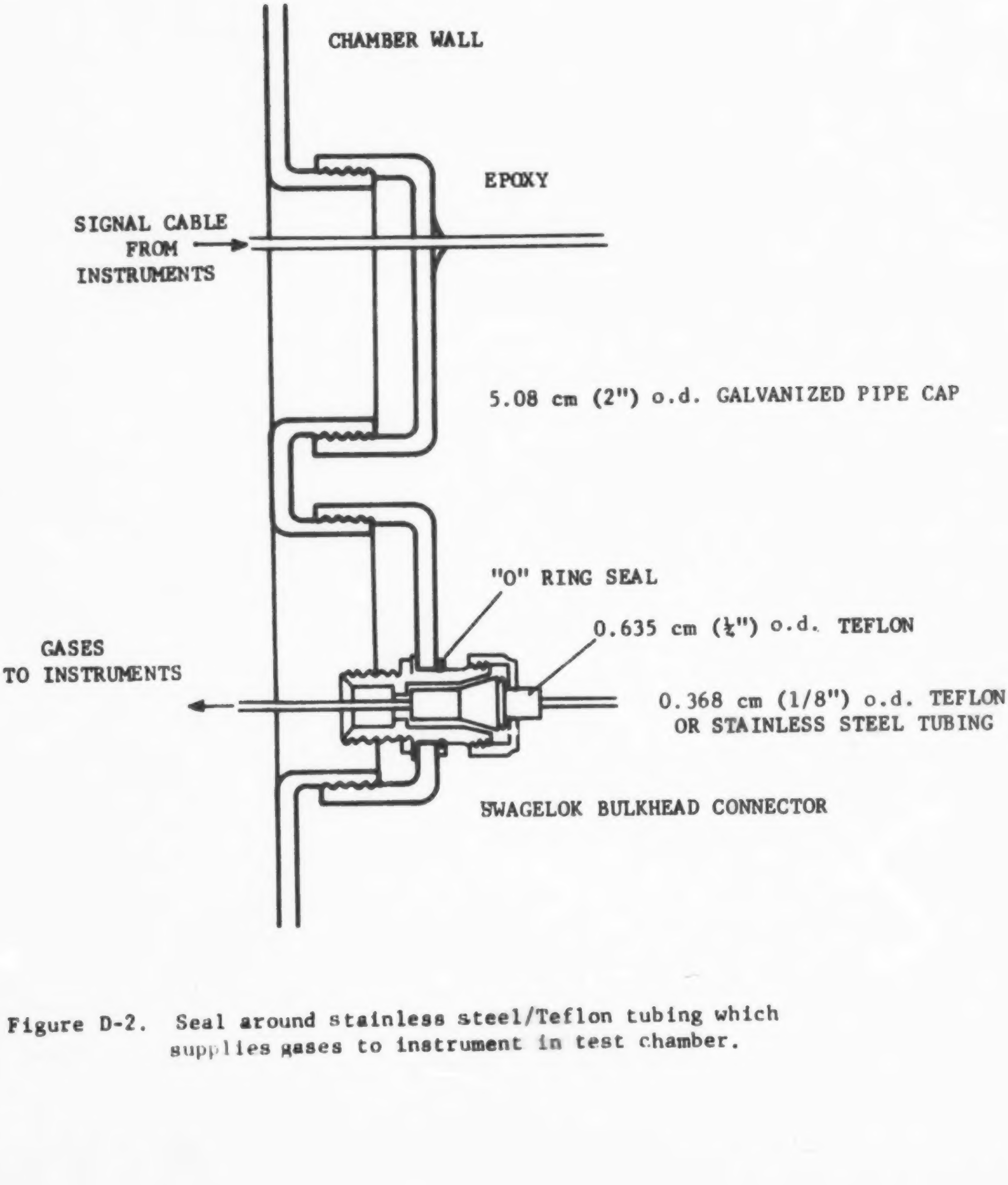

CHAMBER WALL
EPOXY
SIGNAL CABLE FROM INSTRUMENTS
5.08 cm (2") o.d. GALVANIZED PIPE CAP
"O" RING SEAL
0.635 cm (¼") o.d. TEFLON
GASES TO INSTRUMENTS
0.368 cm (1/8") o.d. TEFLON OR STAINLESS STEEL TUBING
SWAGELOK BULKHEAD CONNECTOR

Figure D-2. Seal around stainless steel/Teflon tubing which supplies gases to instrument in test chamber.

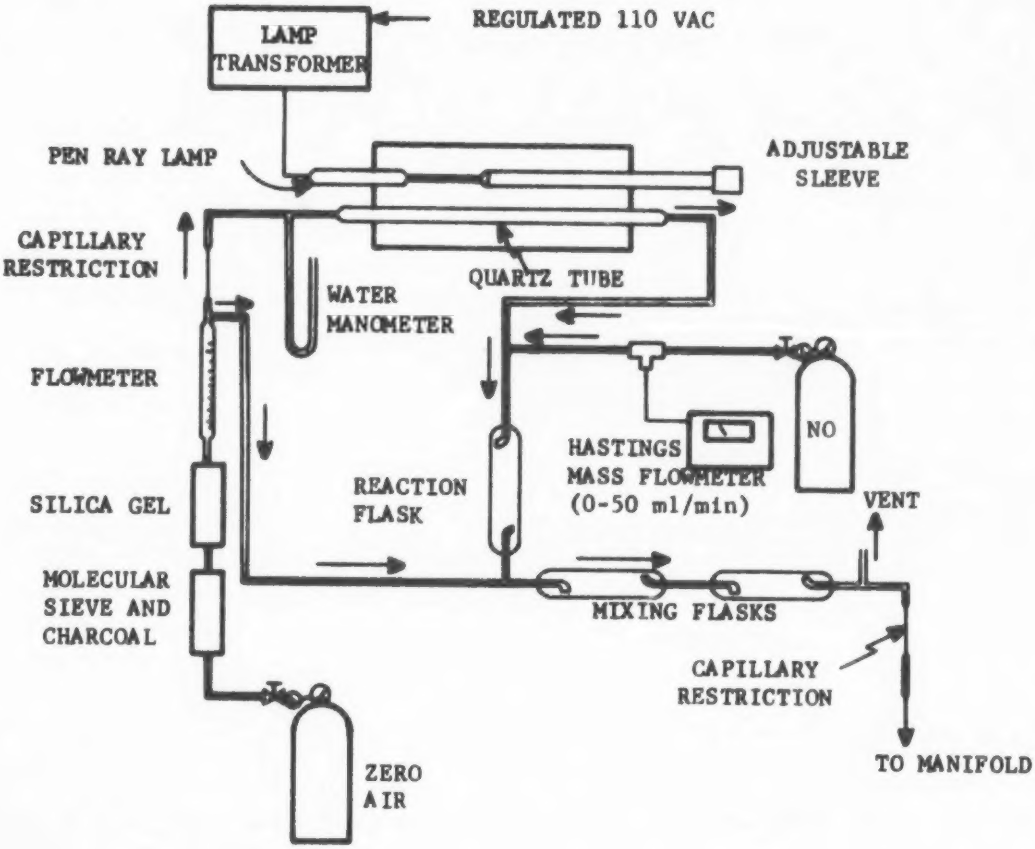

LAMP TRANSFORMER
REGULATED 110 VAC
PEN RAY LAMP
ADJUSTABLE SLEEVE
CAPILLARY RESTRICTION
QUARTZ TUBE
WATER MANOMETER
FLOWMETER
NO
HASTINGS MASS FLOWMETER (0-50 ml/min)
SILICA GEL
REACTION FLASK
VENT
MOLECULAR SIEVE AND CHARCOAL
MIXING FLASKS
CAPILLARY RESTRICTION
TO MANIFOLD
ZERO AIR

Figure D-3. Ozone generator/gas phase titration system for calibration of O_3 and NO-NO_x analyzers.

Provided an excess of NO is maintained, the relationship between NO, O_3, and the concentration of NO_2, in ppm, produced, is determined as follows:

$$C_{NO} = \frac{C_{CYL} \times F_{NO}}{F_T} - C_{O_3} \qquad (2)$$

$$C_{NO_2} = C_{O_3} \qquad (3)$$

where

C_{NO}, C_{NO_2} = Calibration system concentration of NO or NO_2 in ppm

C_{CYL} = Cylinder NO concentration, ppm

F_{NO} = NO flow rate, cc/min

F_T = Total flow through the system, zero air + NO, cc/min

C_{O_3} = O_3 concentration, ppm

The NO concentration supplied by the manufacturer for the pressurized cylinder of NO used in this test, was referenced to equivalent ozone concentrations added during titration. A straight line was drawn through the linear portion of the titration curve and extrapolated to the axis of the curve representing the ozone concentration. The concentration determined by the intercept was considered the O_3 concentration equivalent to the initial diluted NO concentration. The cylinder NO concentration was then determined from the following formula:

$$C'_{CYL} = \frac{C'_{NO}\ F_T}{F_{NO}} \qquad (4)$$

where parameters not previously defined are:

C'_{CYL} = concentration of NO in cylinder as determined from gas titration procedure

C'_{NO} = initial NO concentration from titration system with no O_3 generated, determined from the equivalence point of the O_3 concentration.

Actual values obtained in the titration run during this study were:

C'_{NO} = 0.865 ppm

F_{NO} = 46 cc/min

F_T = 5046 cc/min

Substituting in equation (4) yields

$$C'_{CYL} = \frac{5046 \times 0.865}{46} \text{ ppm} = 94.9 \text{ ppm}$$

The concentration of cylinder NO determined by the titration method agreed to within 10% of the concentration reported by the manufacturer. The discrepancy may in part be due to the age and prior cylinder use, which were not known at the time of this test.

D-4 Test Procedure

The units under test were calibrated several times during the study at ambient conditions of temperature and pressure (25°C and 708 mm Hg). These calibrations were conducted by administering the zero air and span concentrations directly to the sample manifold through the removable by-pass shown in figure D-1. The pressure differential between the manifold and ambient conditions during these tests was determined to be less than 0.6 cm of water. Subsequent calibrations were conducted with the chamber controlled at 25°C and at various simulated altitudes above ambient. During the reduced pressure tests, the sample manifold was maintained at chamber pressure by placing a capillary restriction upstream from the manifold and leaving the downstream end of the manifold open ended into the chamber (refer to fig. D-4). The sample was drawn into the chamber because the chamber was at a vacuum relative to the calibration system which was at ambient. The length of the teflon capillary was adjusted so that the flow drawn into the chamber was 2.5 to 4 ℓ/min. The remainder of the 5 ℓ/min by the calibration system was vented into the room through an unrestricting vent to maintain a constant ambient pressure within the calibration system. This, in effect, provides for a known concentration of the calibration gas (O_3, NO, or NO_2 in this case) to be made available to the instrument at the pressure of interest based on measurements or calibration procedures conducted at ambient pressure. Figure D-4 illustrates the typical pressure and flow conditions during a reduced pressure test with the chamber controlled at a simulated altitude of 3048 meters (10,000 feet).

It was observed that the instruments adjusted much more rapidly to changes in pressure than did the entire system (instrument and calibration system) to changes in concentration. Therefore, these tests consisted of setting the system up for a single calibration gas level input and varying the pressure stepwise over the range being tested. Runs were repeated using the same input concentration levels on different days to determine repeatability. Also, different input concentrations were used to check linearity of the analyzers over the pressure range of interest.

D-5 Results of Tests

Bendix NO-NO_2-NO_x Analyzer

The response of the chemiluminescent NO-NO_2-NO_x analyzer to two different constant concentration levels of NO under varying environmental pressure is shown in figure D-5. The data appears to be very repeatable with no more scatter than found when the instrument is operated under normal laboratory conditions.

A graph showing the percentage correction necessary to convert readings taken at any altitude up to 5500 meters (18,000 feet) to the actual concentration is shown in figure D-6. This graph was used for determining the correction factors for adjusting the data taken at various

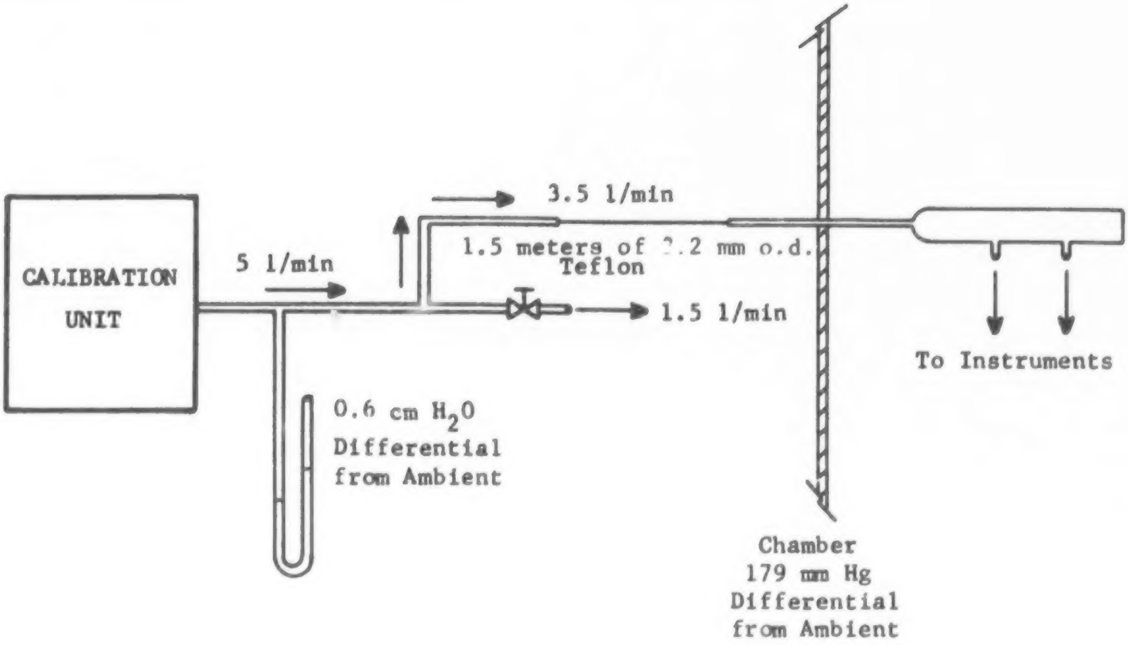

CALIBRATION UNIT
5 l/min
3.5 l/min
1.5 meters of 3.2 mm o.d. Teflon
1.5 l/min
To Instruments
0.6 cm H_2O Differential from Ambient
Chamber 179 mm Hg Differential from Ambient

Figure D-4. Typical pressure and flow conditions for chamber setting at simulated altitude of 3048 meters (10k feet).

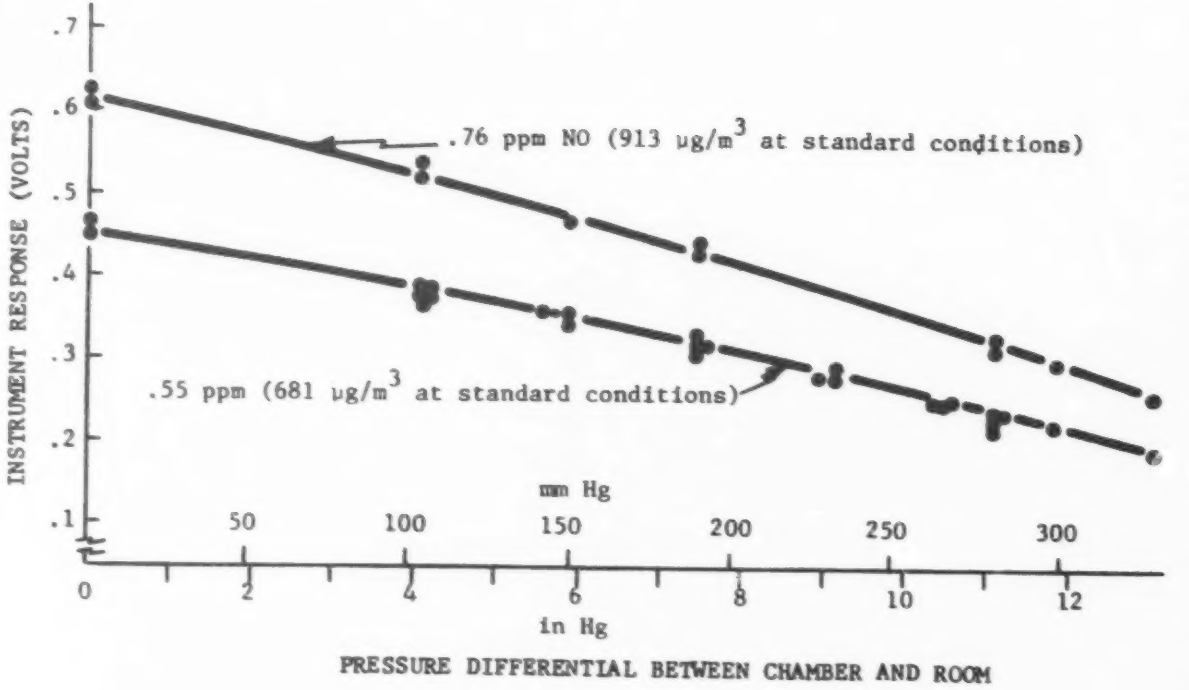


Figure D-5. Response of Bendix NO_x analyzer vs pressure for two concentrations.

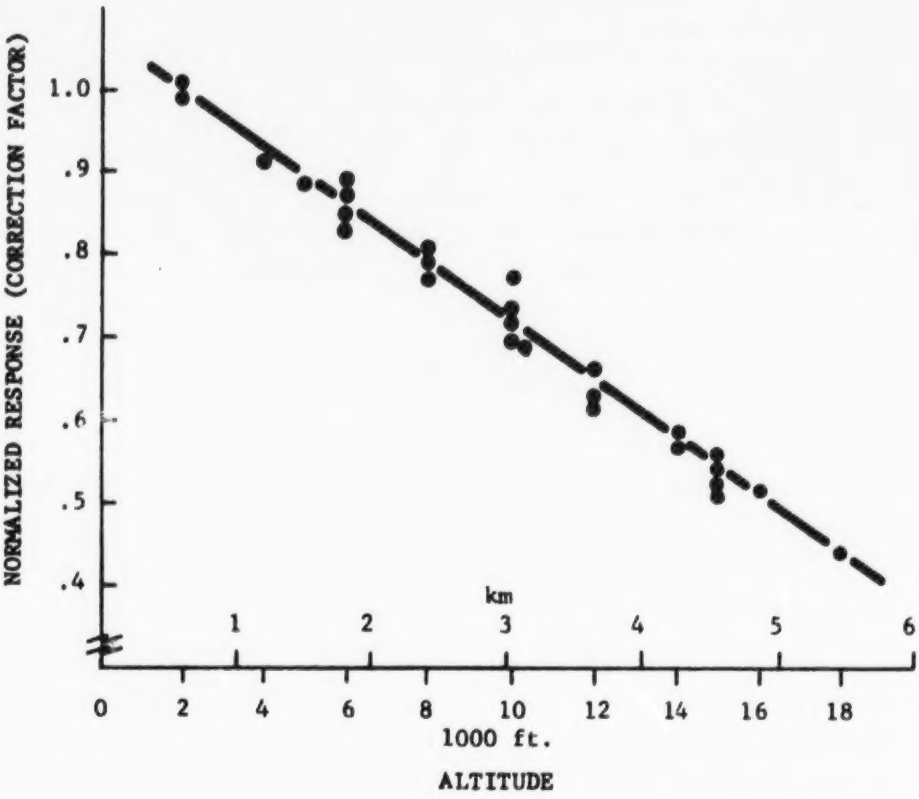


Figure D-6. Correction factor for Bendix NO_x analyzer to compensate for changes in altitude. (To use, divide reading obtained from instrument by number read from graph for the altitude needed.)

altitudes to a common altitude for comparison. Note that the approximate linearity of this curve is derived by plotting instrument response with altitude on the ordinate instead of pressure.

During these tests the volumetric ratio of NO to air as expressed in ppm is held constant. At conditions of sea level and 25°C, 1 ppm of NO is 1225 $\mu g/m^3$. At altitudes above sea level this figure drops proportionally with the density of air. It follows then that for each ppm input the actual concentration in $\mu g/m^3$[*] is 1225 at a pressure of 760 mm Hg and drops linearly to zero at 0 mm Hg. Therefore for a concentration of 0.555 ppm of NO the mass per volume would be 681 $\mu g/m^3$ at sea level and drop linearly to zero at 0 mm Hg. This type of response, the ideal mass per volume response, is shown in figure D-7 along with the actual response of the instrument to 0.555 ppm input. The two appear to track reasonably over the range of pressure 760 to 500 mm Hg with less than 10% error. This would be expected since the output of the instrument is directly proportional to the amount of light given off by a reaction of ozone and NO. Consequently, all operating conditions being equal, the instrument response should be directly proportional to the amount of mass of NO being sampled by the instrument. Hence it is expected that the output would fall off nearly linearly.

There is, however, an additional variable and that is the variation in sample flow rate in the instrument. If the instrument response is proportional to the mass of NO entering the sample inlet, then the response drop-off due to decreasing pressure would be further compounded by any accompanying decrease in volumetric flow. Variations in volumetric flow rate with changing pressure were determined experimentally both in the test chamber and in the aircraft. Attempts at mathematically predicting the response of the instrument based on the assumption that instrument response depended solely on the mass of sample air[**] being drawn through yielded a significant difference between the predicted and

---

[*] The use of $\mu g/m^3$ here should not be taken as a cubic meter at standard conditions. Here the m^3 refers to a cubic meter at the pressure of the sample.

[**] Mass of air as it varied with air density and flow rate.

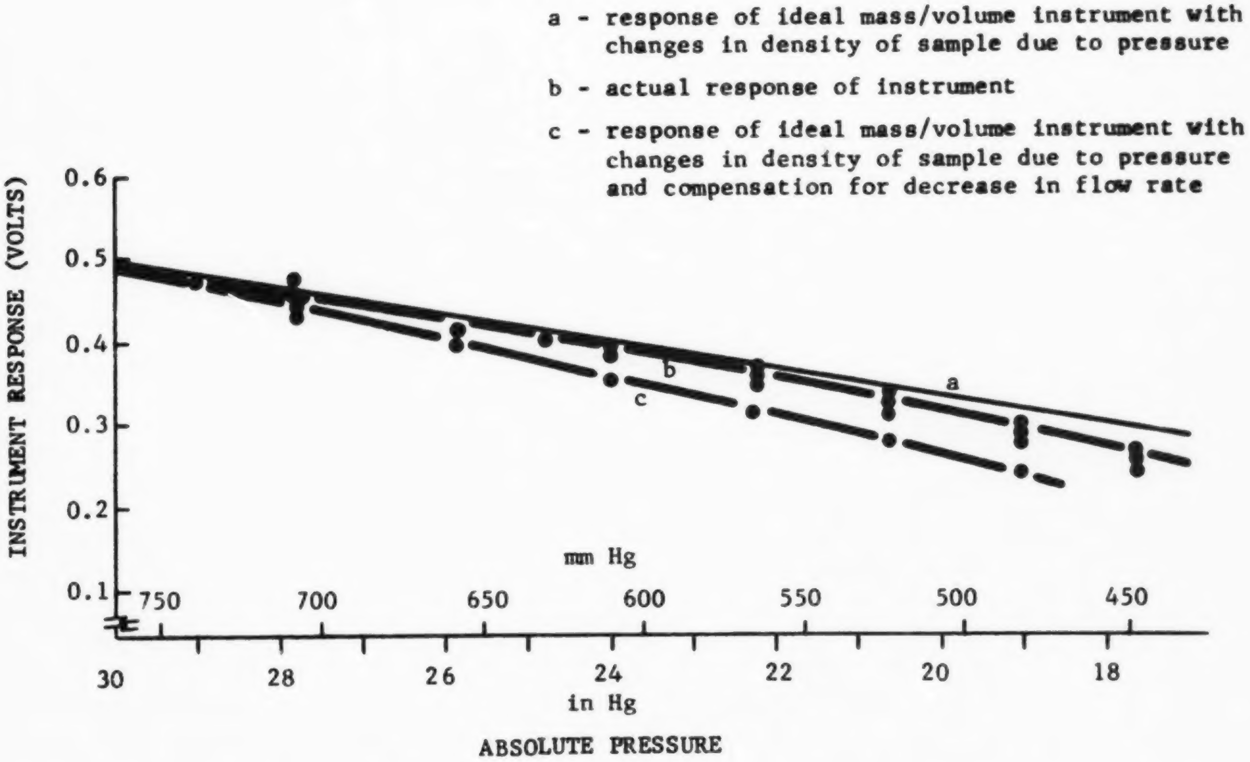


Figure D-7. Response of Bendix NO_x analyzer compared to ideal mass per unit volume instrument.

measured response. The difference (error) was actually greater than the difference computed for the case discussed in the preceding paragraph where the assumption was that the instrument response varied only with changes in sample flow due to changing ambient pressure with no compensation for varying sample volumetric flow rate. Curve C in Figure D-7 illustrates the predicted instrument response with compensation made for changes in volumetric flow and air density.

A possible reason for this is variations in pressure in the reaction chamber where the ozone and NO react. In the tests reported here, no means were included for controlling the reaction chamber pressure in the instrument or even accurately measuring it. A small vacuum gauge indicated that the actual chamber pressure did change a small amount but no significant quantitative data were taken. A more meaningful test of the NO detection technique would result from controlling the actual reaction chamber pressure. However, the tests performed here more closely simulate actual operating conditions where the instrument and its vacuum pump are placed aboard an aircraft and no attempt is made to control the reaction chamber pressure, or volumetric flow rate. It should be noted that the change in volumetric flow rate with altitude was found to be quite repeatable and was checked on each flight at the altitude(s) of interest.

Analyzer response to calibrated span concentrations of NO_2 are illustrated in figure D-8. The measurement of NO_2 with a chemiluminescent analyzer involves the same processes as the measurement of NO with only one difference — the conversion of NO_2 to NO by means of a catalytic converter. Therefore, to analyze the NO_2 response, the data were examined to see how the response to NO_2 compared to the response to NO. To do this the ratio of NO_2 to NO response was computed for various pressures for one input concentration (.555 ppm NO and .316 ppm NO_2). Figure D-9 shows the ratio for different ambient pressure conditions. The data indicates a trend toward lower converter efficiencies at lower absolute pressures (higher altitudes); however the variation on all runs was less than 8% up to 4572 meters or 15,000 feet (down to 429 mm Hg). At altitudes of [illegible]000 feet or less the average decrease in efficiency appeared to be approximately 3-5%. Therefore, the same correction factors for NO data were used with NO_2 data for compensation of altitude effects.

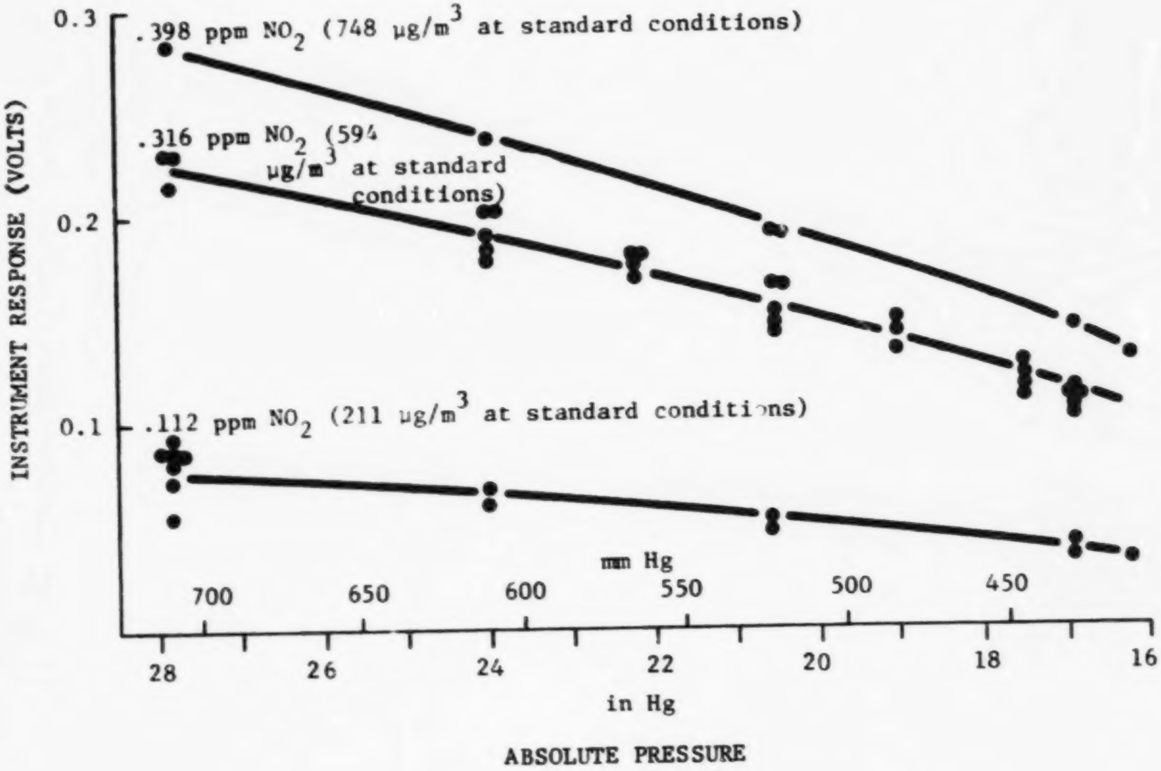


Figure D-8. Response of Bendix NO_x analyzer to 3 constant concentrations with varying pressure.

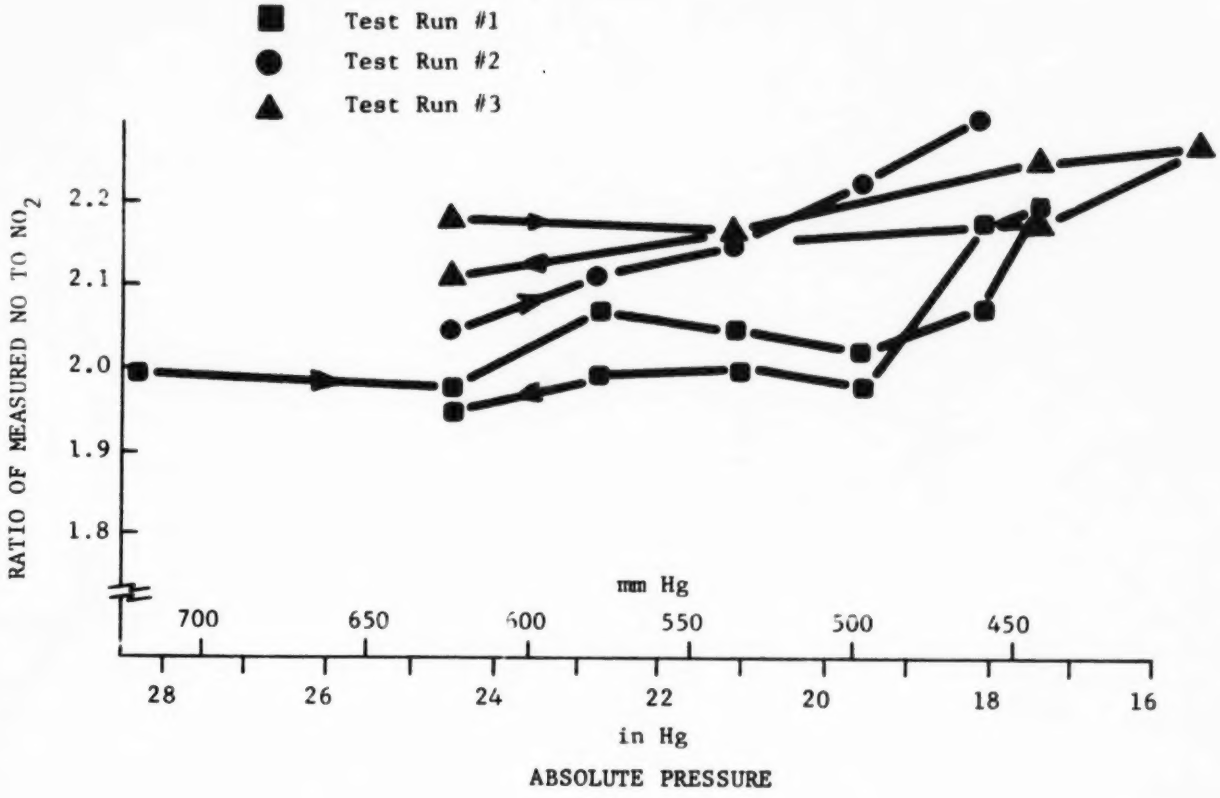


Figure D-9. Ratio of NO to NO_2 response for constant concentration with varying pressure.

Bendix Ozone Analyzer

The response of the gas phase chemiluminescent ozone analyzer to span concentrations for various environmental pressures is shown in figure D-10.

Daily measurements were normalized to an initial reading of unity at ambient pressure conditions in the laboratory. Then the results of all runs were plotted on the same graph. This graph, shown in figure D-11, shows a decrease in response almost directly with the density of the sample air. (Sample air density is the broken line of the same graph.) The graph also shows repeatability of the instrument response; however, verification of the altitude factors by means of an inflight calibration is recommended at frequent intervals during airborne measurement programs.

RTI Ozone Monitor

The RTI solid phase chemiluminescent ozone monitor uses a rhodamine-B disk for sensing ozone. Since the disk response is dependent on the recent history of the disk, a fixed level calibration ozone generator was built into the unit and is energized periodically. The standard cycle in the instrument tested consists of four parts, each of 30 seconds duration: (1) purge with clean air, (2) sample from ambient (measure cycle), (3) purge again, and (4) calibration gas from internal ozone generator (calibrate cycle). The measured concentration is then computed from the ratio of the disk response to ozone in ambient air to its response to the ozone calibration concentration. Therefore, the instrument response with altitude is solely dependent on the behavior of the internal ozone generator with altitude.

The RTI instrument was tested at a different time than the other two instruments, but the same test setup and equipment were used. A constant concentration of ozone was generated external to the pressure chamber and applied to the instrument input. The instrument response to this input (measure response) and the response to the internal generator were recorded. The measure response alone indicates the response of this disk under the varying pressure and pressure-induced flow conditions. The disk response does not significantly affect the accuracy of the instrument

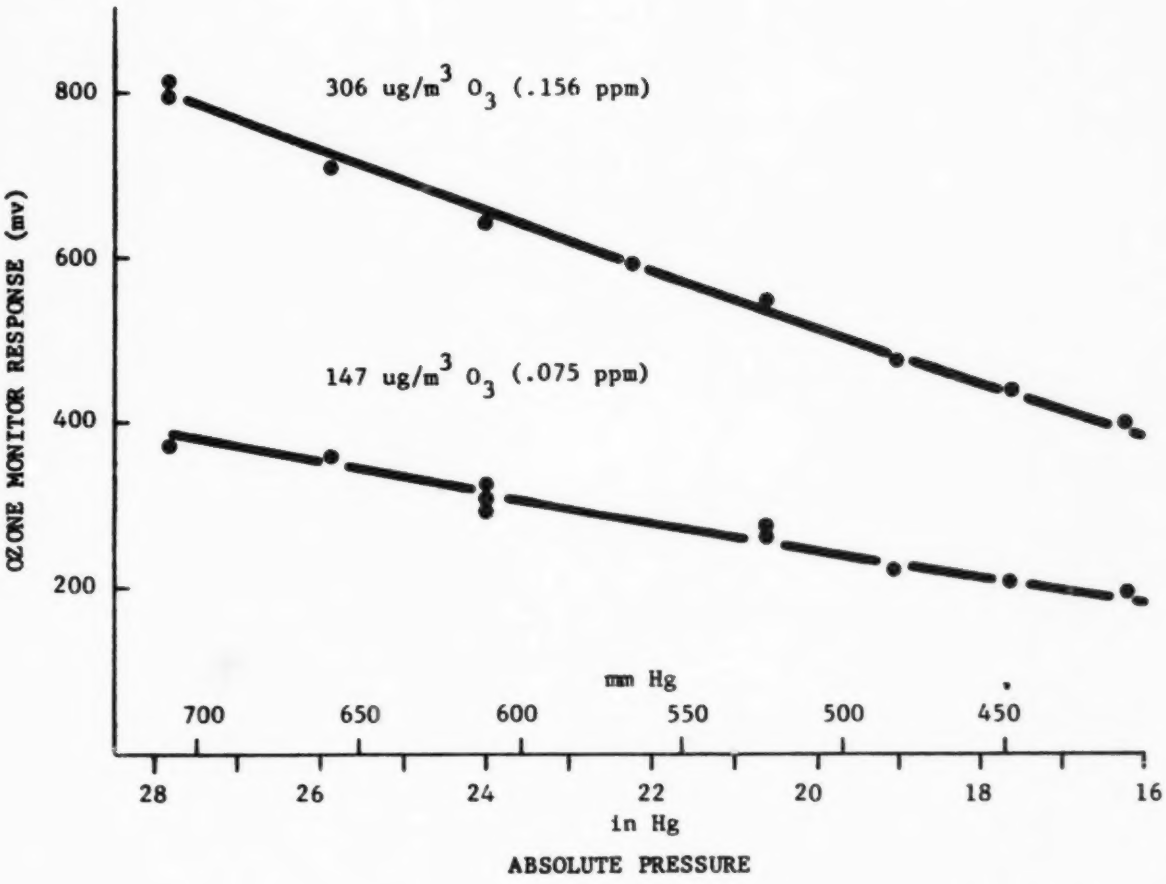


Figure D-10. Response of Bendix O_3 analyzer to constant concentration with varying pressure.

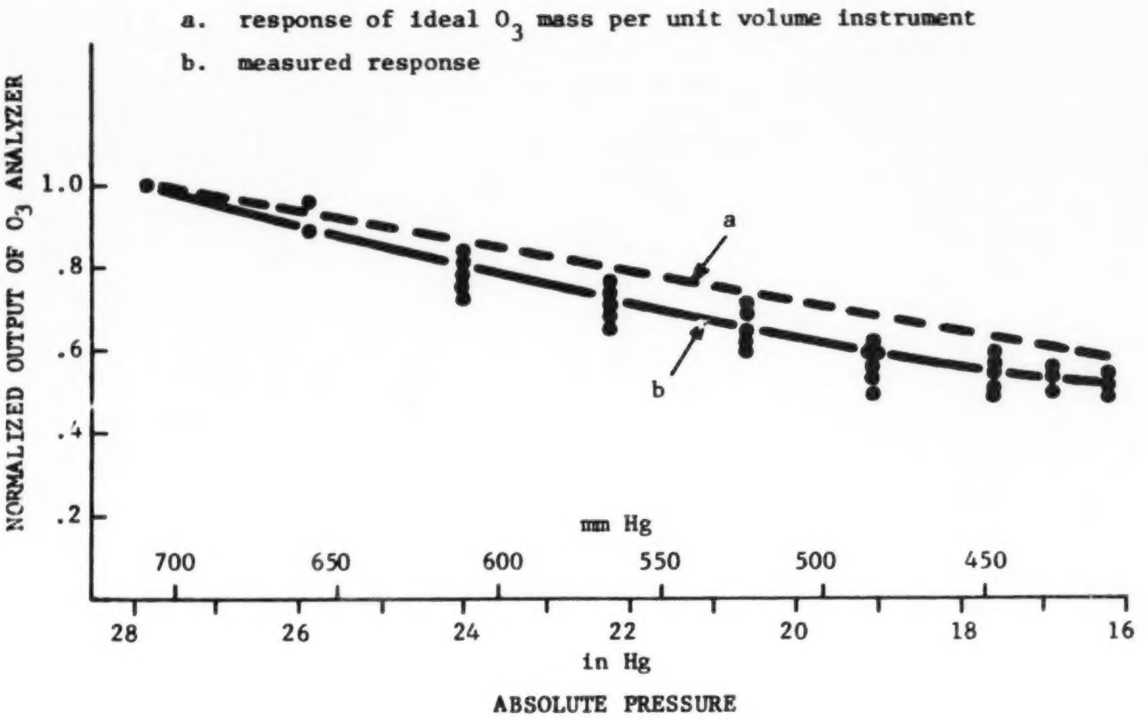


Figure D-11. Normalized response of Bendix O_3 analyzer to varying pressures.

since the measured concentration is always determined from the ratio of the sample response to calibration response. Consequently, the measure response data are not plotted here.

Since measure response is the response to an externally generated concentration of ozone, the behavior of the internal generator may be determined for varying pressure conditions by computing the ratio of calibration response to measure response. The total instrument response, however, is the ratio of measure response to calibration response and is, therefore, the reciprocal of the above function. Consequently, this ratio, normalized to 1.0 at ambient conditions, is shown in figure D-12.

The response of the RTI instrument falls off with increasing pressure as did the other instruments tested. This decrease in response is due to an increase in the ppm output of the ozone generator at higher altitudes (lower pressures) produced by at least two separate mechanisms: (1) reduced volumetric flow rate through generator due to lower vacuum pump efficiency at higher altitudes, and (2) reduced pressure between the ultraviolet light source and the quartz tube containing the air to be exposed to the light for ozone generation (lower pressure means fewer ozone molecules which absorb ultraviolet light). Still another source of variation of ozone output from the generator is the change in pressure within the quartz chamber where the clean air sample is irradiated with UV to produce ozone. The overall instrument response curve (fig. D-12) was used for compensation of values obtained in the aircraft for altitude effects. This is accomplished by reading the value corresponding to the altitude of interest from the graph and dividing it into the reading obtained from the instrument.

The instrument performed in a repeatable manner during all tests. All the mechanisms assumed to cause variation in performance with pressure were relatively time invariant (i.e., not changing with age and condition of the instrument) except flow rates. To prevent an unnoticed change in the vacuum pump efficiency at higher altitudes from changing the altitude response characteristics and causing erroneous data to be recorded, flow rates were monitored by means of a soap bubble flow meter during the tests and later during the data flights.

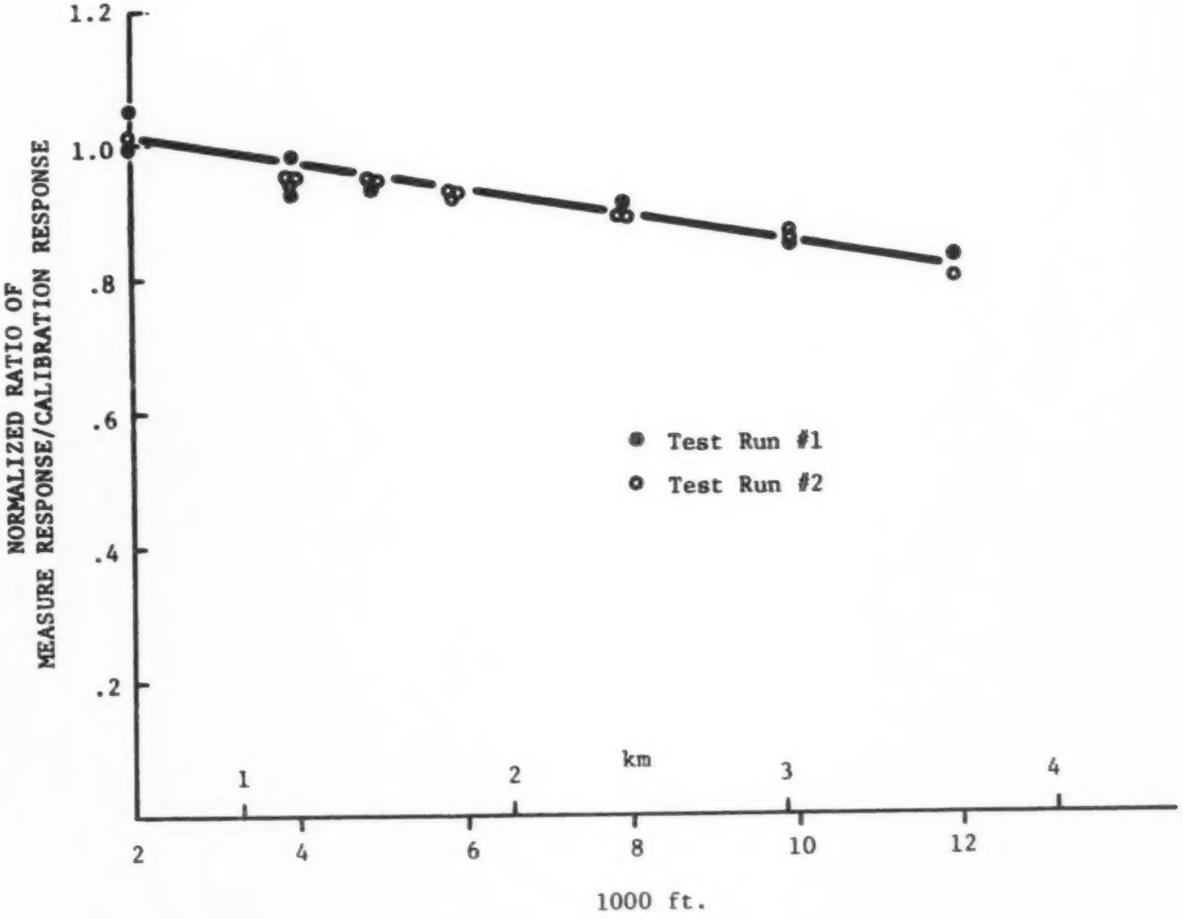


Figure D-12. Response of RTI O_3 instrument vs altitude

APPENDIX E

OPERATIONAL PROCEDURES FOR AIRCRAFT INSTRUMENTATION

E-1. General

The specific operational procedures for the aircraft instrumentation are listed below. An introductory paragraph describing generally what each sequence of operations is designed to accomplish is given prior to each checklist. Procedures are included for:

1. Preflight Checklist,
2. Ozone Analyzer Calibration:
    Ozone Generator Verification (Calibration Unit),
    Ozone Instrument Calibration,
3. NO-NO_2-NO_x Analyzer Calibration,
    NO-NO_2 Source Verification (Calibration Unit),
    NO-NO_2-NO_x Instrument Calibration.

E-2. Preflight Checklist for Aircraft Operation

1. Conduct required calibrations and ambient air checks.

2. Connect glass manifold to line coming from sample port in lower right front of cabin and connect both ozone and NO_x instruments to manifold.

3. Check instruments for proper mode of operation.

Ozone Instrument

a. Lamp current--9 ma. Setting about 90.
b. Mode control--sample 1.
c. Rotameter--about 2.
d. Shutter--open.
e. Sensitivity--10^{-7}
f. F.S. output--4.
adjust to give output of about 1/4 to 1/2 of full scale.
g. Time constant norm on calibrate signal.
h. Zero adjust--set to zero.
i. High voltage setting--990V.

Preceding page blank

NO_x Meter

a. Set oxygen pressure to 20.
b. Check cylinder pressure for reading of 25 on output gauge.
c. Check ozone generator light--should be ON.
d. Check valve switch--should be NO-NO_x-NO_x.
e. Check mode switch--should be on ambient.
f. Set all PPM range switches to 0.S.
g. Turn pump and power switches ON.

Recorder Panel

a. Set top switch on control panel to zero full counterclockwise.
b. Turn all recorders on.
c. Set range on top 4 recorders to 0-IV; on bottom recorder to 0-10 mV.
d. Set zero adjust for 10 percent scale.
e. Set all chart speeds to 8 in/hr.
f. Put pens down.
g. Turn DVM on and set range for 2 VDC.

Power Panel

a. Switch 1 should be set for ground power.
b. Priority 1 and 2 power--ON. Lights should be ON.
c. Timer pump OFF--center pos.

Manifold

a. Check placement of 2 Teflon tubes and temperature sensor. They should be at least 15.24 cm inside Teflon pipe air inlet. Make sure they are secure.

Temperature Gauge

a. Function switch should be an ambient and meter should read approximate cabin temperature.

E-3. Ozone Analyzer Calibration

The ozone analyzer calibration will be checked before each flight by injecting a known concentration of ozone into the sample manifold from a one-point generator. This will establish the behavior of the instrument on the ground. Results of experimental tests at the beginning of the program and at approximately its midpoint will be used to determine the instrument behavioral variations with altitude and, therefore, what corrections must be made in the data taken at different altitudes.

1. Verification of Ozone Generator (External)

The base station ozone analyzer shall be used to routinely determine the concentration output of the portable system used to generate ozone construction in the aircraft. The ozone instrument then is in effect a transfer standard used to calibrate the calibration box from a standard ozone generator whose output has been referenced to the neutral-buffered KI method.

The ozone generator is a dual pen-ray lamp unit with adjustable sleeves covering the lamps. The setup procedure for operating the unit is as follows:

a. Connect to 110 VAC outlet.

b. Switch ON and adjust lamp current to 15 ma. Allow to stabilize overnight.

c. Connect air supply from breathing quality air cylinder to air inlet.

d. Close pressure adjust valve.

e. Adjust air valve for a flow indication on the large rotameter of 6.7 (TOB).

f. Set sleeves to first marked setting.

g. Connect sample manifold to glass ball joint on front of instrument and connect ozone analyzer to first opening in manifold.

h. Allow enough time for analyzer to stabilize, indicated by constant trace on strip-chart recorders or constant output concentration levels by station minicomputer.

i. Read generator output on teletype.

2. Routine Calibration of Ozone Analyzer in Aircraft

Immediately before every flight, the portable calibration unit shall be used to calibrate the aircraft ozone analyzer. Additional verification of ozone analyzer performance and aircraft manifold system checks can be accomplished by comparison of aircraft ambient readings with base station readings while on the ground and during a low pass at the beginning and end of each flight.

The procedure for calibrating the analyzer is as follows:

a. Set up calibration system and connect to aircraft analyzer as described in steps 1-8 under verification of ozone generator.

b. Note the height of the instrument responses to the internal calibration unit and the external calibration unit. Responses are measured from the baseline determined during the purge cycle to the average response after the instrument has stabilized during each phase of the cycle. Illustration of measurement procedures is given in section 3.2.4.1.

c. Compute the magnitude of the internal calibration level from the following formula:

$$C_{int} = C_{gen} \frac{C}{M}$$

where

C_{int} is the ozone concentration output by the internal calibration unit.

C_{gen} is the ozone concentration output by the portable calibration unit.

M is the instrument response while in the measure phase of its cycle.

C is the instrument response while in the calibrate phase of its cycle.

d. Return the instrument to ambient air by connecting it to the sample inlet brought in from above the aircraft through the window.

e. Allow the instrument to stabilize and note readings and time. Compute concentration from formula

$$C_{amb} = C_{int} \frac{M}{C}$$

where

C_{omb} is the measure ozone level in the ambient air. Readings may be compared with base station readings to verify operation of instruments.

f. After the aircraft is airborne long enough to insure operation of all instrumentation, the aircraft will fly a low-pass flight over the base station as low as safely possible. The ozone instrument should be in the measure mode as the pass is made. The time is marked on the strip-chart recorder, and the value computed for later comparison.

g. After flight, connect instrument sample input to top of flowmeter and measure sample flow rate. Compare with data from previous runs.

E-4. Nitrogen Oxides Analyzer Calibration

The known concentration of NO for instrument calibration is derived by a dilution of NO from a known calibration gas cylinder with air. Although, by careful flow measurement and control, the resulting concentration may be computed, checks may be made using the base station NO_x analyzer to check for any calibration system (or analyzer) malfunctions. Such a check should be carried out every 2 weeks as soon as possible after base-station calibration.

1. Verification of NO_x Calibration Unit

The NO_x calibration unit produces a known quantity of NO by diluting a known NO calibration gas to a concentration within the range of normal atmospheric values. The ozone generator used for calibrating the ozone analyzer is included in the equipment to allow production of NO_2 from NO for calibration of that channel of the analyzer. The performance of the calibration unit may be checked by connecting it to the instrument in the base station as soon as possible after a calibration of the station. This should verify its operation. In order to accomplish this, the following steps will be carried out:

a. Set up the calibration unit as described in steps 1 through 7 under "Verification of Ozone Generator (External)."

b. Connect the calibration gas to the NO inlet on the calibration system. Close the NO valve.

c. Connect a vacuum pump to the fitting on the regulator and pump it down. Close the cylinder valve and repeat the process several times.

d. Adjust the NO valve for a reading of 4.5 (top of ball) on the small rotameter. This represents a flow of 28.2 cc/min at the Clinton County elevation.

e. Set the ozone generator sleeves to their first notch.

f. Connect NO_x analyzer to manifold on output of cal unit and allow time for instrument stabilization. Instrument should have the following readings:

for NO

$$C_{NO_2} = C_{gen} \times 1880$$

for NO_2

$$C_{NO} = (C_{NO_x} - C_{gen}) \times 1220$$

where

C_{NO} is the calibration system output for NO in ppm,

C_{gen} is the ozone output of the generator in ppm,

C_{NO_2} is the calibration system output for NO_2 in ppm,

C_{NO_x} is the concentration of the calibration gas. After dilution by a factor of 28.2/5028.2.

g. If readings do not compare, check operation of instrument, calibration of the NO cylinder, or flow of gases in calibration unit.

2. Routine Calibration of NO_x Analyzer

On the days on which a flight is to be run, a zero and span calibration shall be performed on the NO_x analyzer before takeoff. First, the zero module is connected to the instrument, and the zero adjust potentiometers are adjusted for zero output. Next, the one-point cal unit is connected to the analyzer, and the span controls are set.

The specific instructions for calibrating the units are as follows:

a. Make sure the NO_x analyzer and the calibration unit lamp have been running for a day continuously prior to starting the calibration. Check oxygen supply and vacuum pump for operation. Set scale on 0-0.5 ppm for NO, NO_2, and NO_x.

b. Plug in zero module and turn unit on.

c. Disconnect NO_x analyzer from manifold and connect to zero module. Allow instrument to stabilize.

d. Connect a Digital Voltmeter to the NO position and insure that the short jumpers from the control panel are connected to the DVM.

e. Adjust the NO zero adjust potentiometers until a reading of zero is obtained on the DVM.

f. Repeat steps 4 and 5 for the NO_2 and NO_x channels.

g. Disconnect the zero module from the NO_x analyzer and connect the analyzer to the calibration unit through a manifold.

h. Set up the cal unit as done in the verification of its operation. Set the ozone generator sleeves to the first notch and allow everything to stabilize.

i. Compute the concentrations of NO, NO_2 and NO_x from

$$C_{NO_x} = \frac{28.2}{5028.2} (C_{cyL})$$

$$C_{NO} = C'_{NO} - C_{GEN}$$

$$C_{NO_2} = C_{GEN}$$

where all concentrations are in PPM and

C_{NO_x} is the concentration of cal gas from the cylinder after dilution with air,

C_{NO} is the concentration of NO output,

C_{NO_2} is the concentration of NO_2 output,

C_{GEN} is the output concentration of the ozone generator,

C_{cyL} is the concentration of the NO calibration gas cylinder.

j. From these concentrations compute the expected response of the instrument and set the span potentiometers to obtain that response.

k. Reconnect the manifold to a sample lower and the NO_x analyzer to it. Then compare readings of ambient levels with those recorded in the base station.

l. Disconnect NO cylinder from cal unit and allow unit to run to an hour with ozone lamp ON to flush system out.

m. After flight has been completed, connect top of bubble flowmeter to sample inlet and measure flow while on ground. Record value and check for any change since past runs.

APPENDIX F

AIR PARCEL TRAJECTORIES

AIR PARCEL TRAJECTORIES

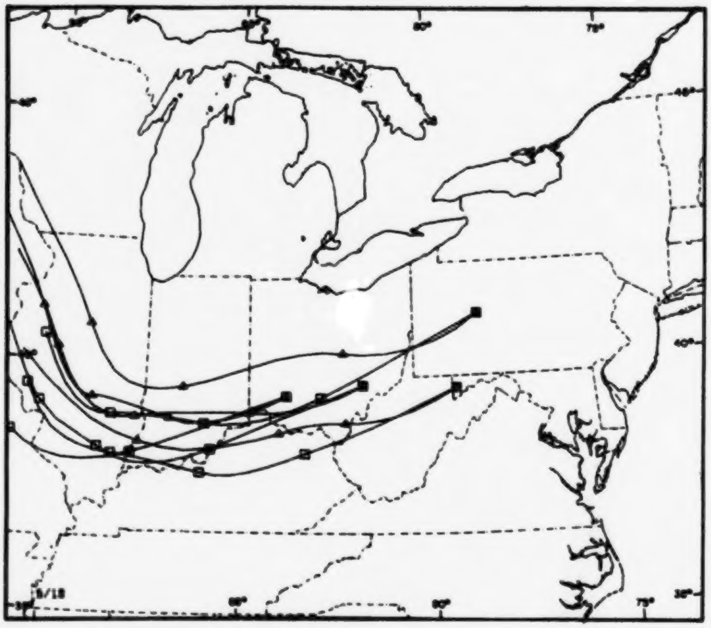
3000 FEET MSL

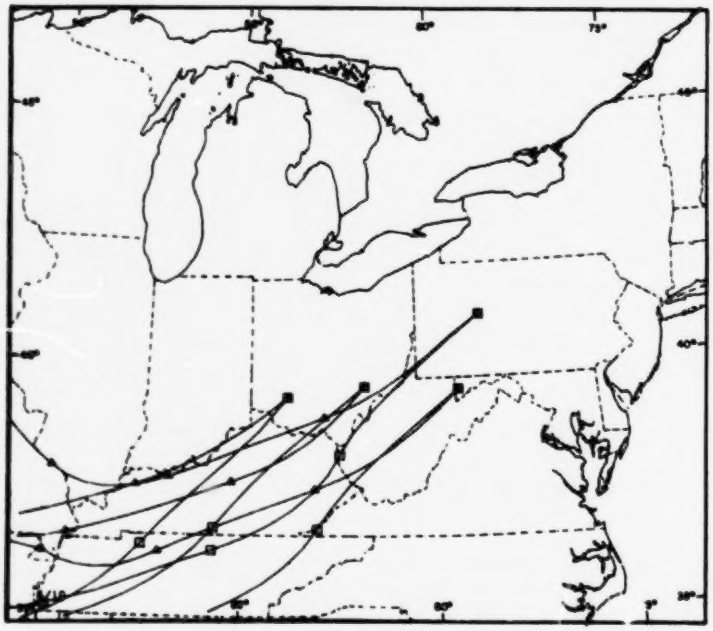
June 18 to September 1, 1974

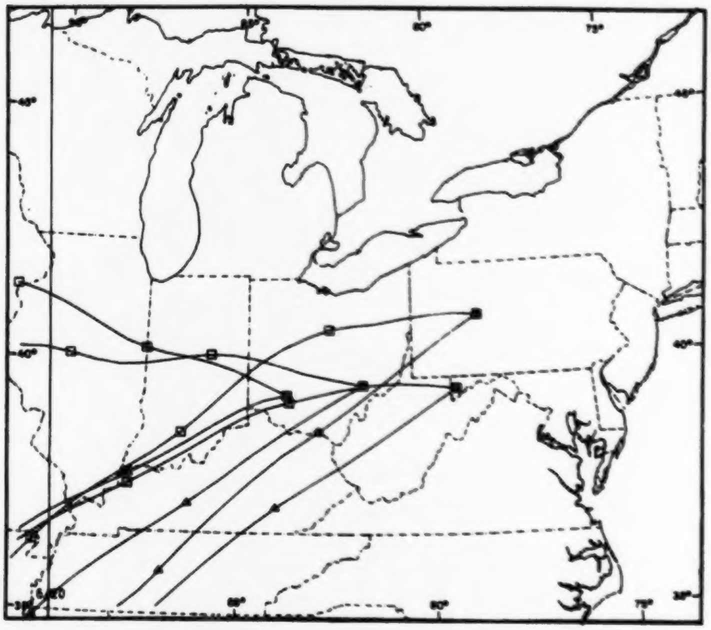
for Air Arriving at
Garrett County, Maryland
DuBois, Pennsylvania
Morgan County, Ohio
Wilmington, Ohio

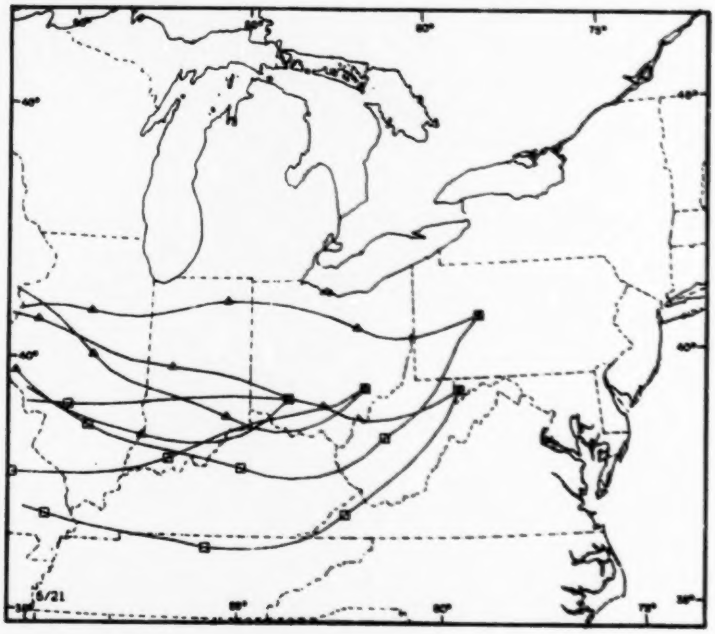
Twelve-hour positions prior to arrival are indicated by a triangle (Δ) for those air parcels arriving at 0000 GMT and by a square (☐) for those arriving at 1200 GMT.

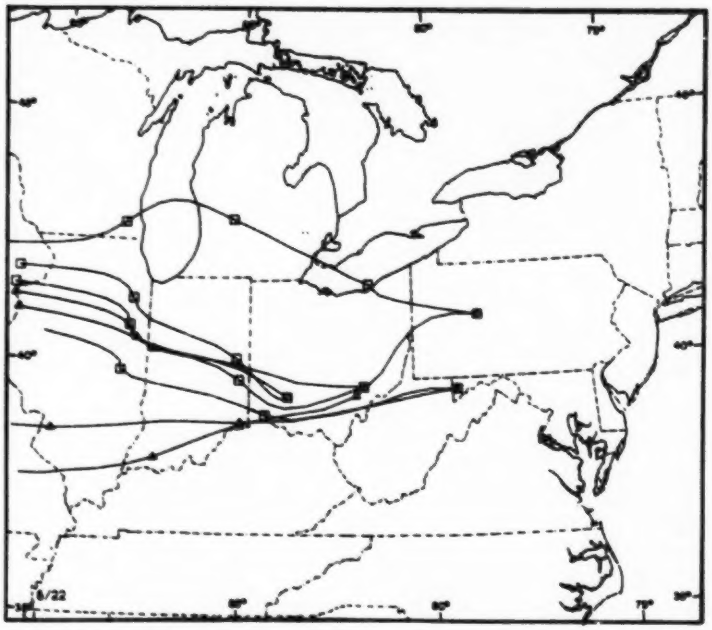
An overlay is provided to help identify locations.

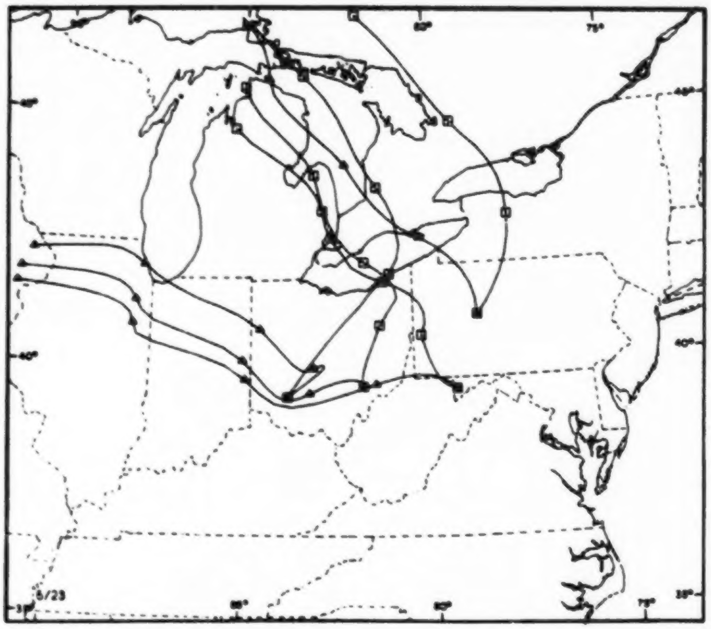

80°
75°
45°
40°
5/18
85°
80°
75°
30°

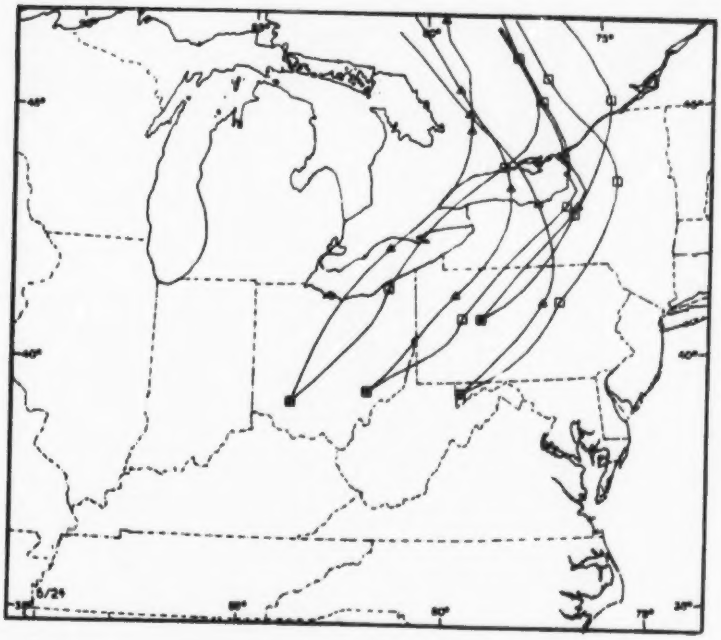

80°
75°
45°
40°
85°
80°
30°


90°
85°
80°
75°
45°
40°
35°
6/20

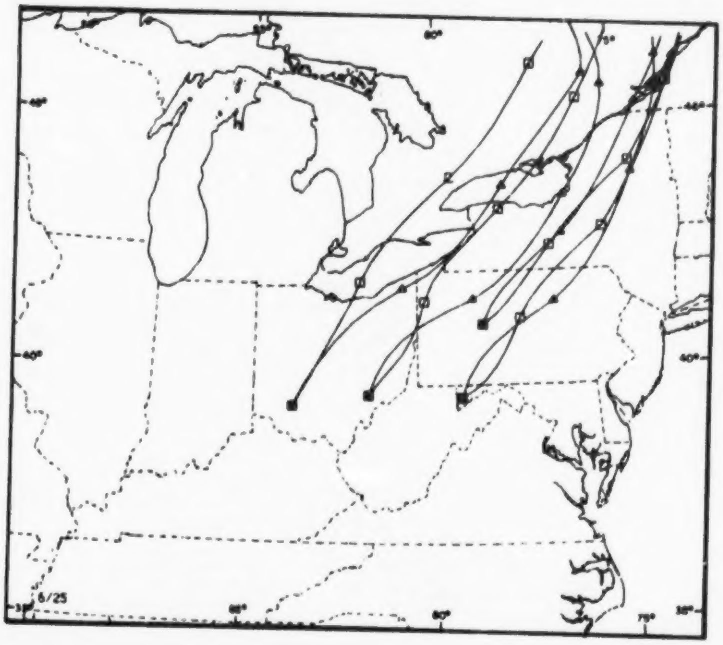

90°
85°
80°
75°
45°
40°
35°
6/21


80°
75°
45°
40°
6/22
35°
85°
80°
75°
35°

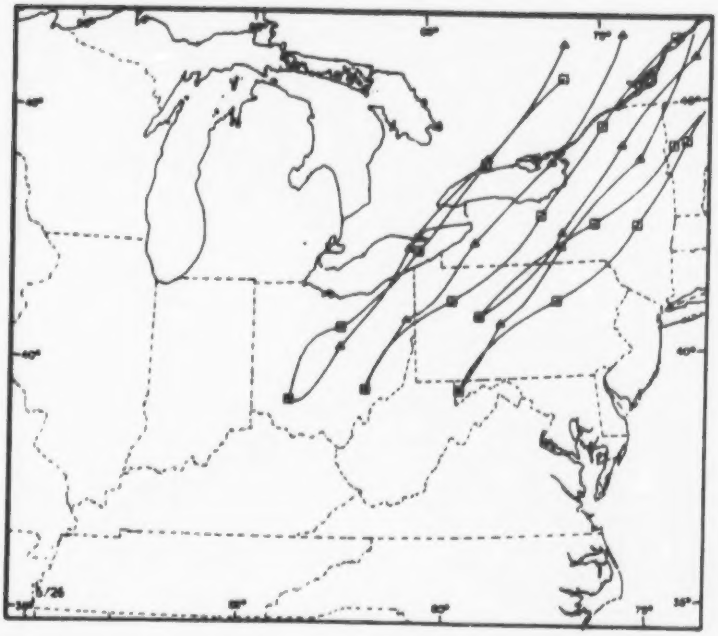

80°
75°
45°
40°
6/23
35°
85°
80°
75°
35°

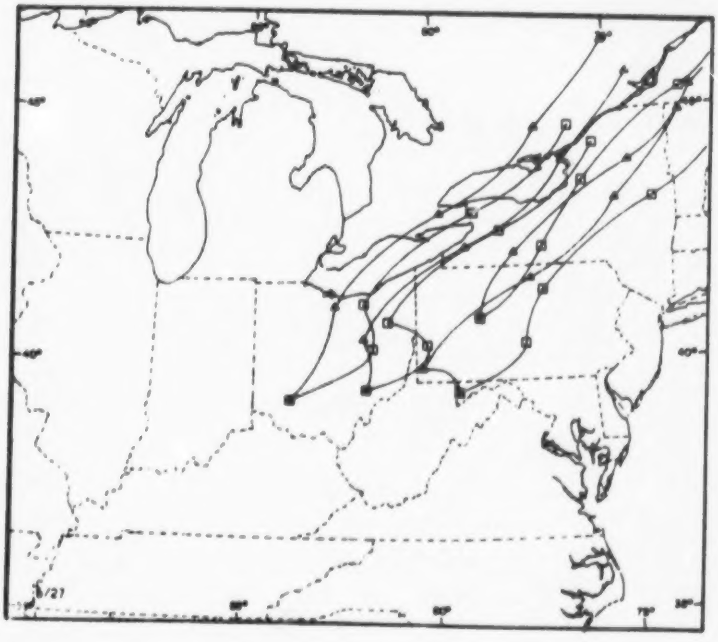


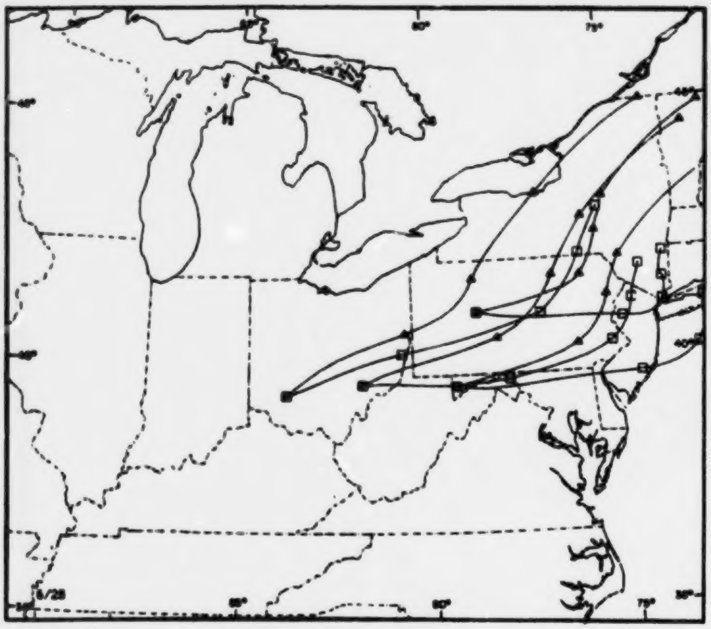
45°
40°
6/24
35°
85°
80°
75°

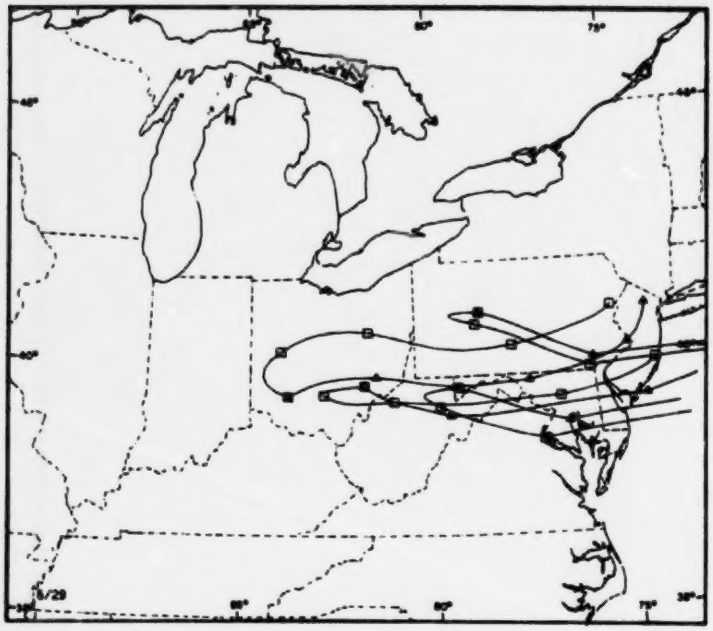


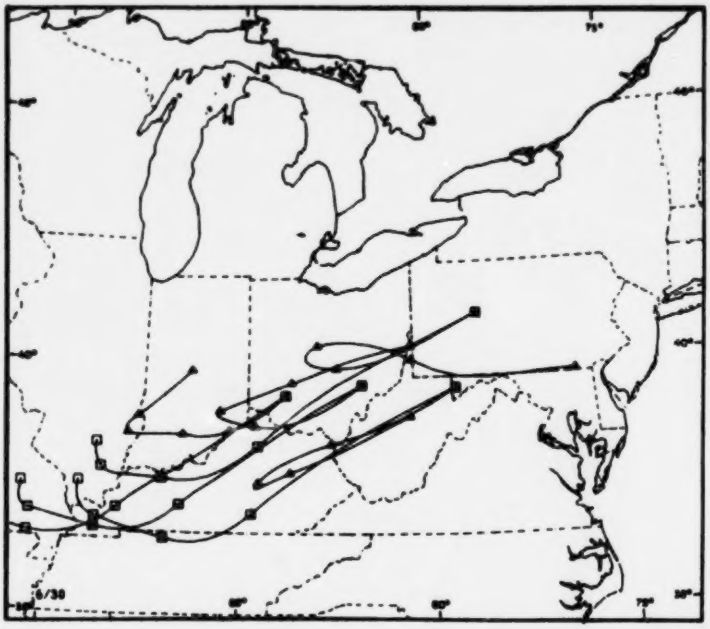
45°
40°
6/25
35°
85°
80°
75°

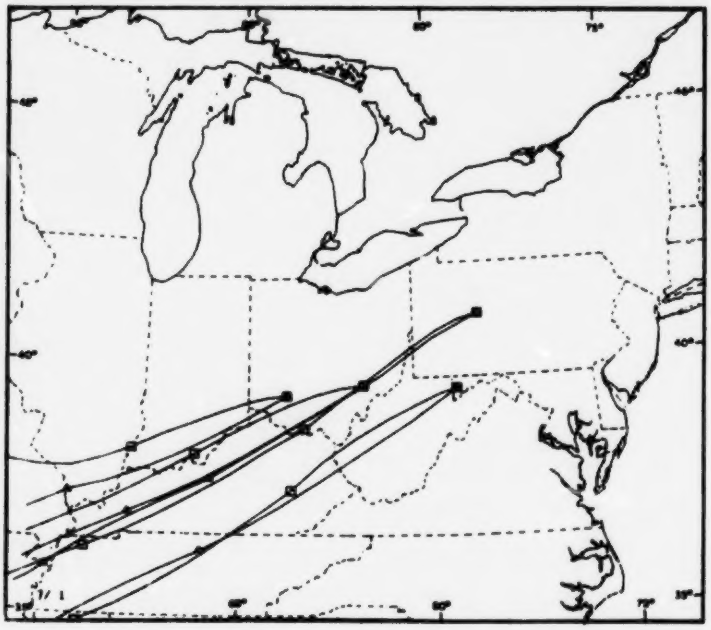

80°
75°
45°
40°
5/26
35°
85°
80°
75°
35°

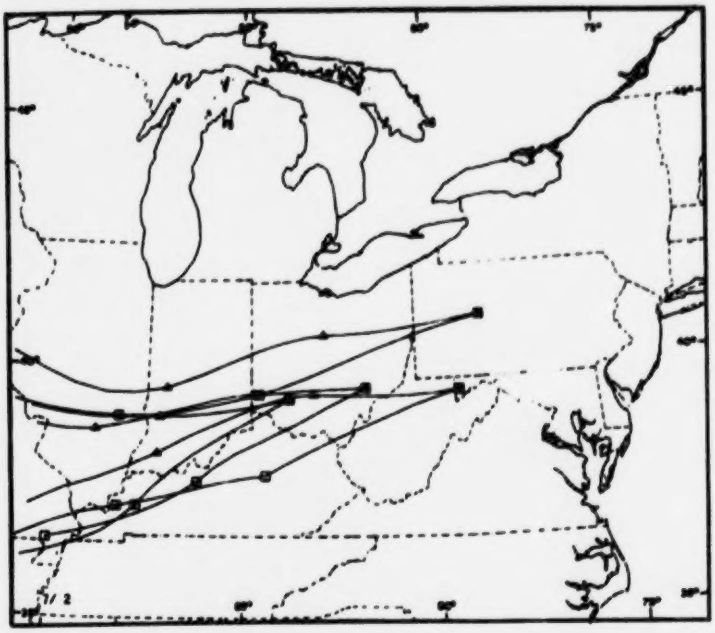

80°
75°
45°
40°
5/27
85°
80°
75°
35°

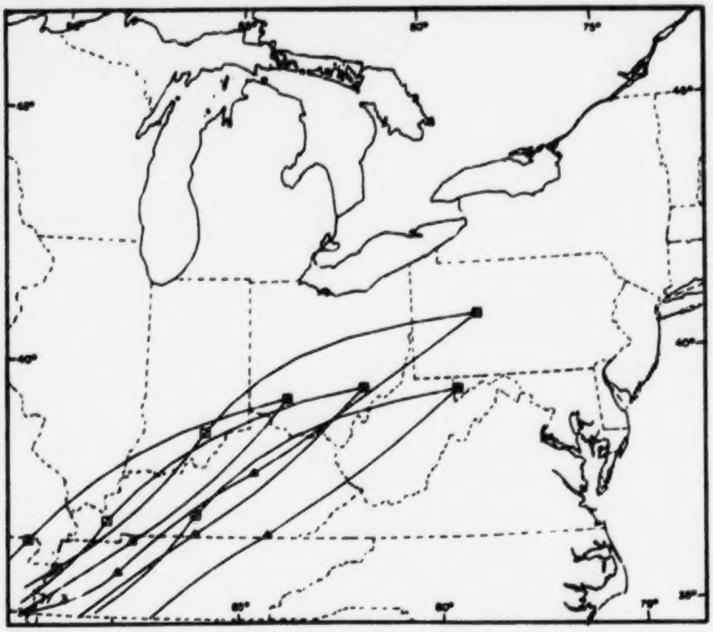

6/28
85°
80°
75°
45°
40°
35°

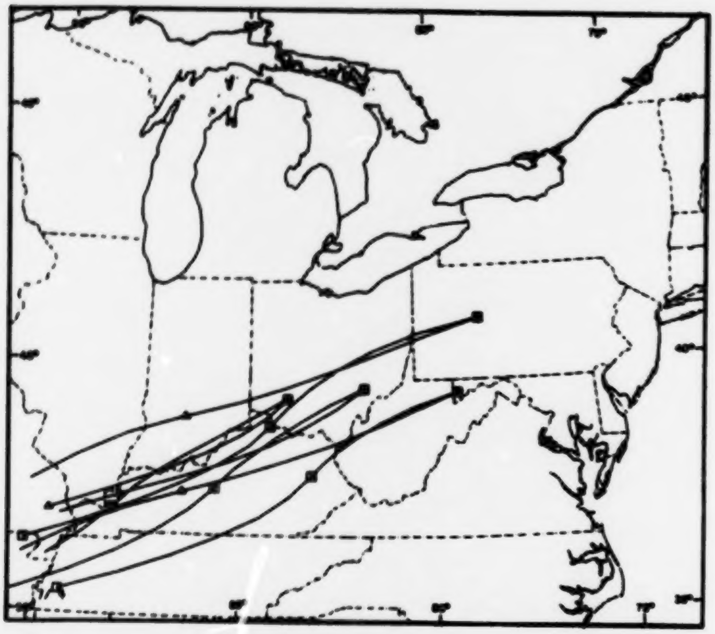

6/29
85°
80°
75°
45°
40°
35°

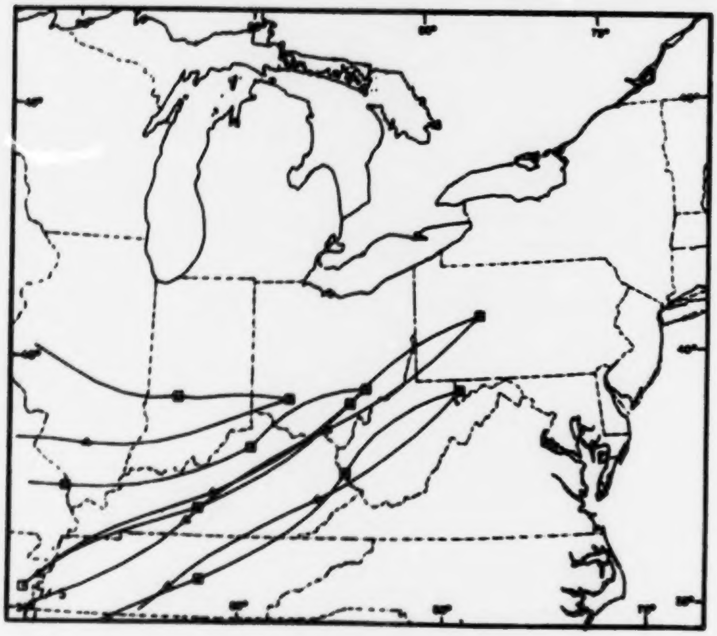

80°
75°
45°
40°
35°
6/30

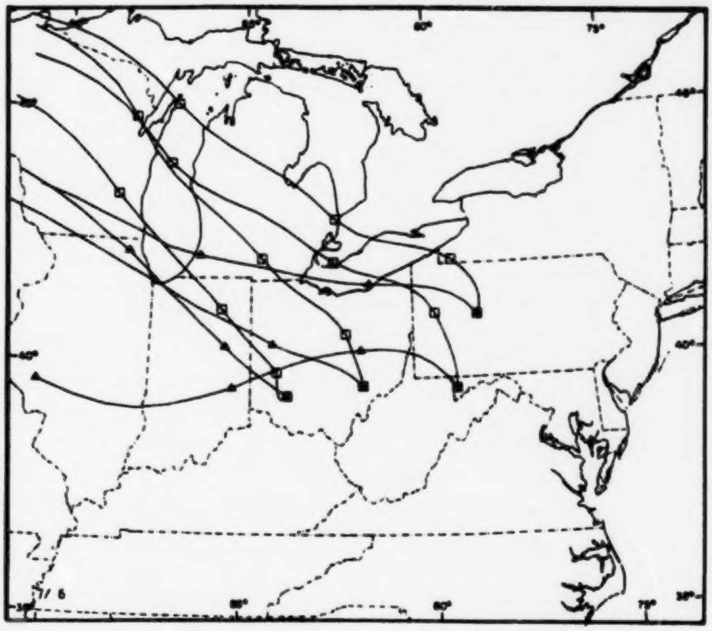

80°
75°
45°
40°
35°
7/ 1

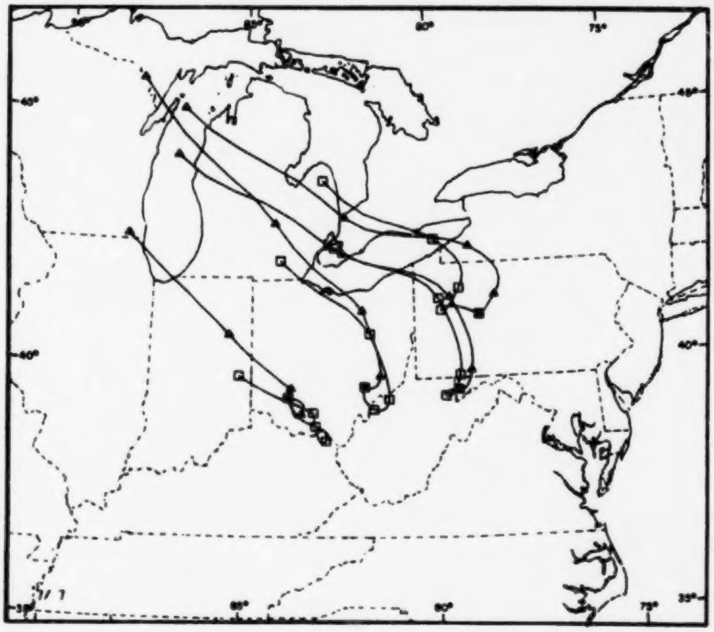

7/ 2

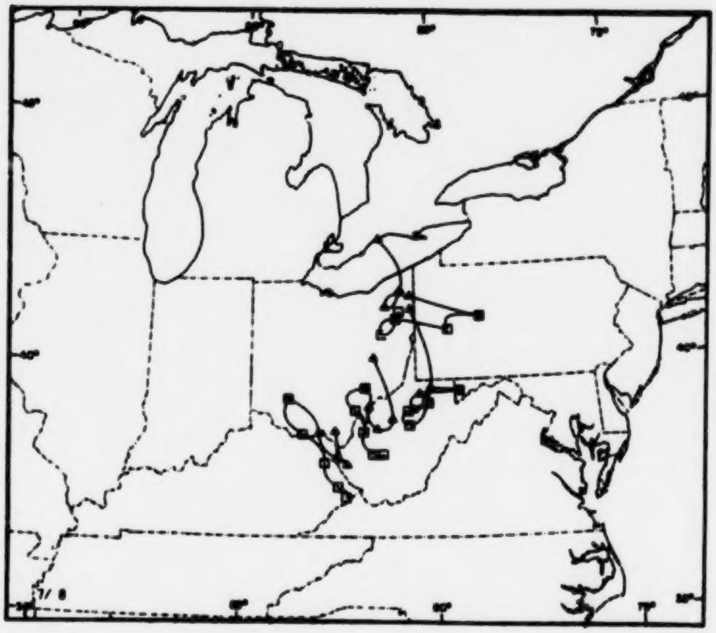




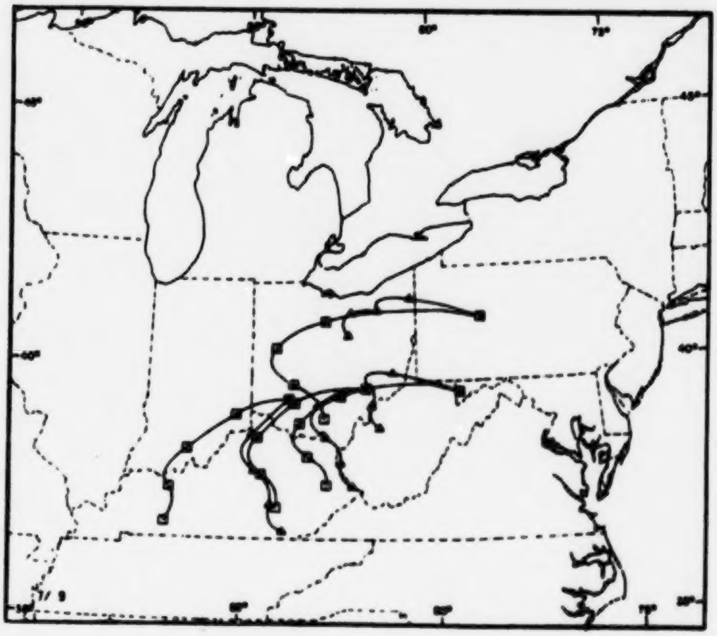



85°
80°
75°
45°
40°
35°
5/ 6

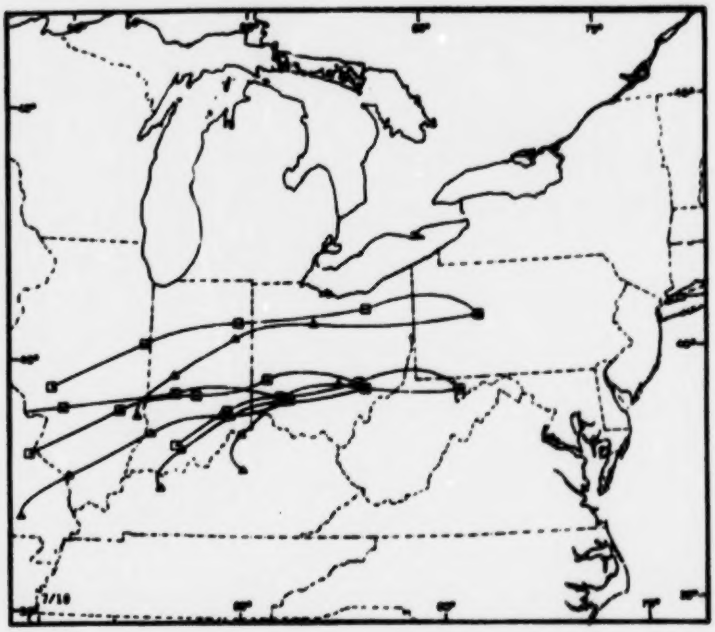

90°
85°
80°
75°
45°
40°
35°
5/ 7



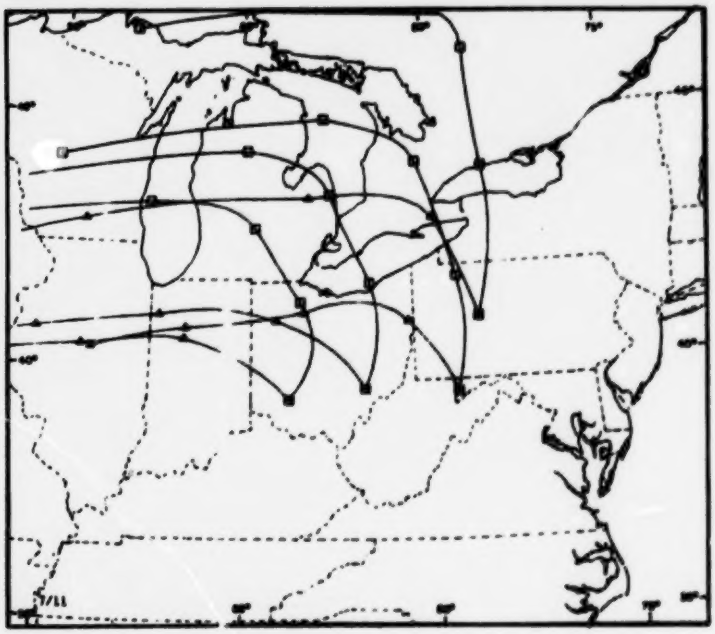
7/ 8



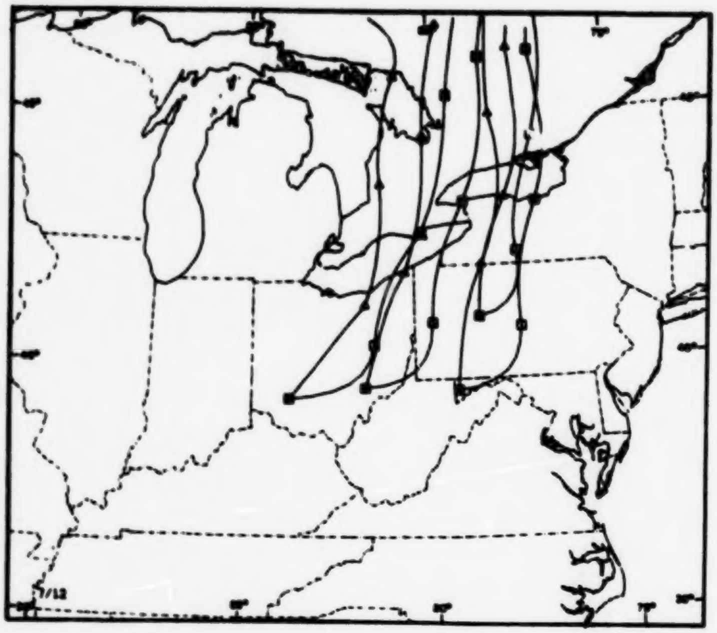
7/ 9

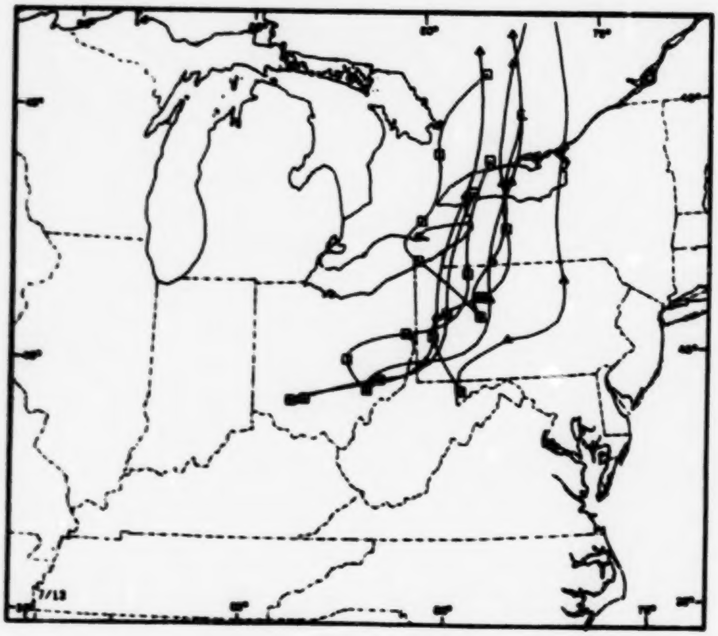


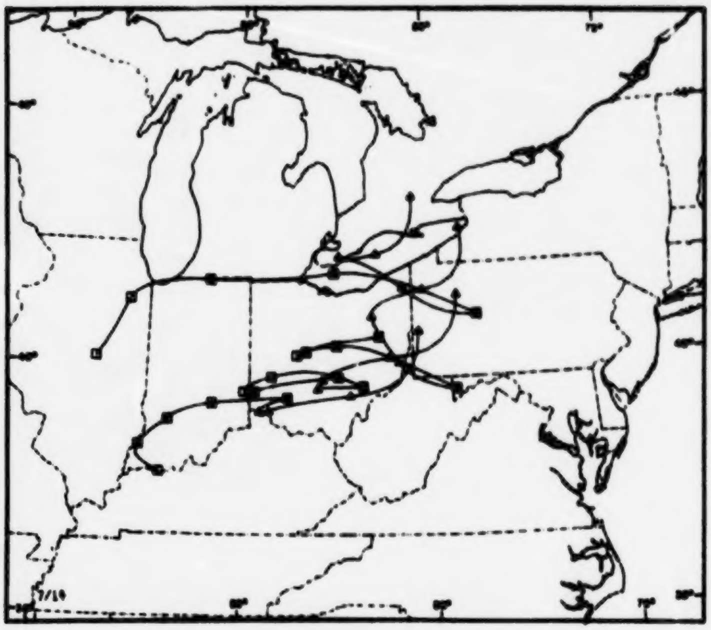
7/10

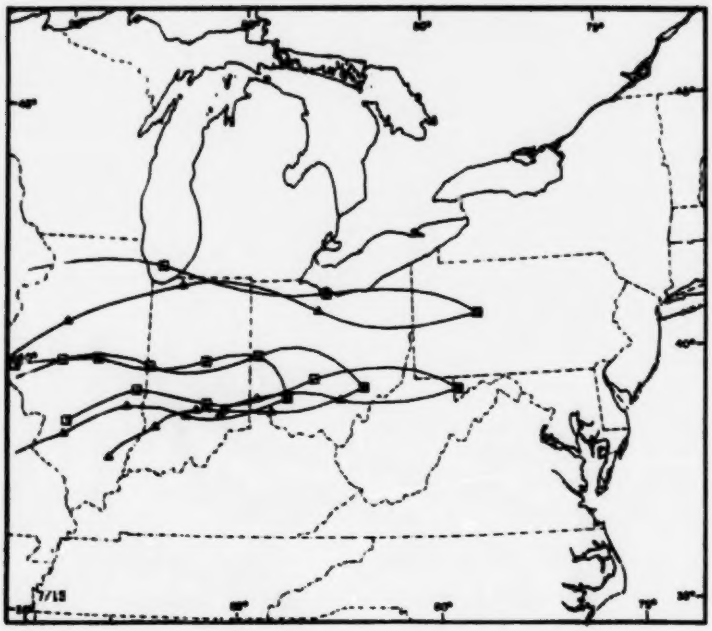


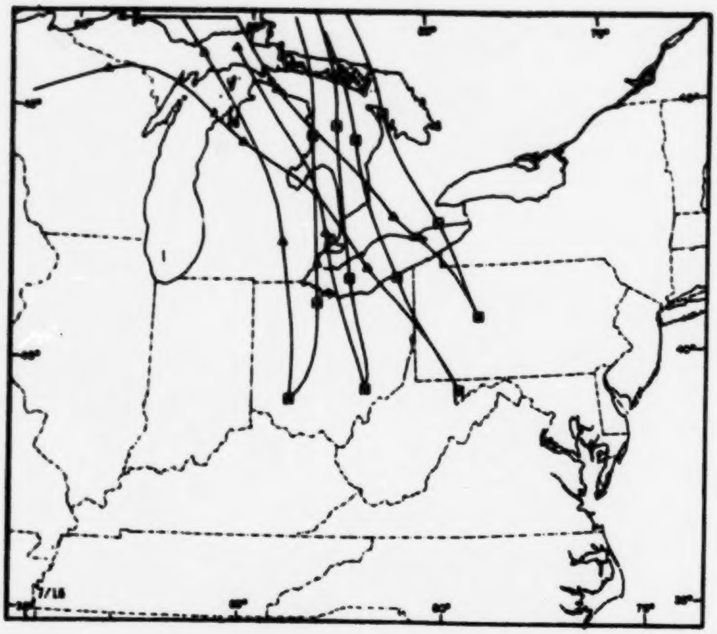
7/11

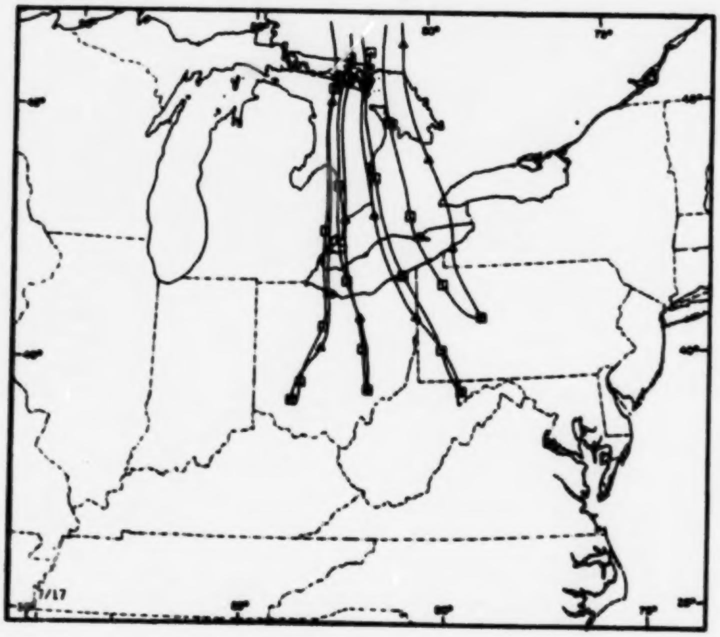

7/12

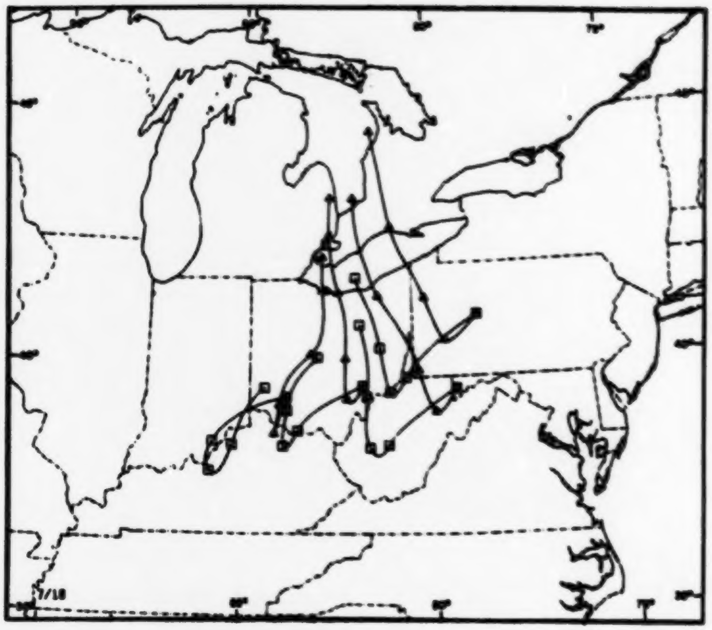

7/12

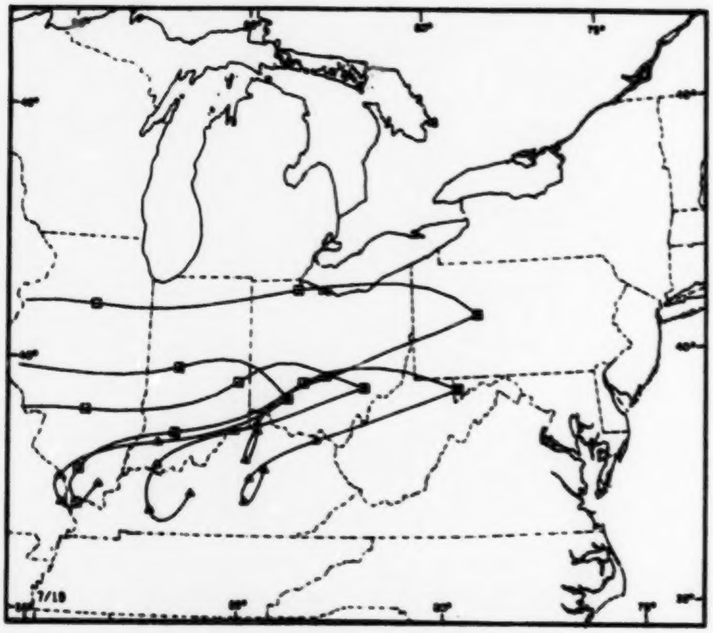

7/14

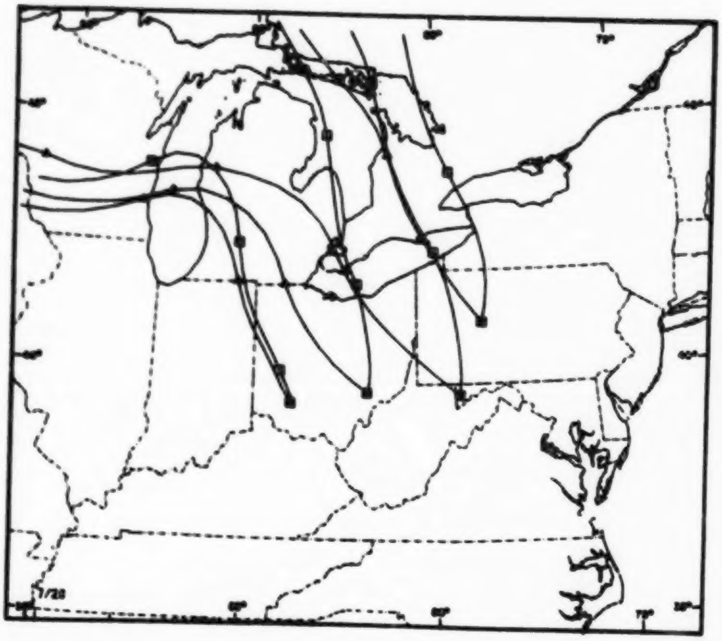

7/15

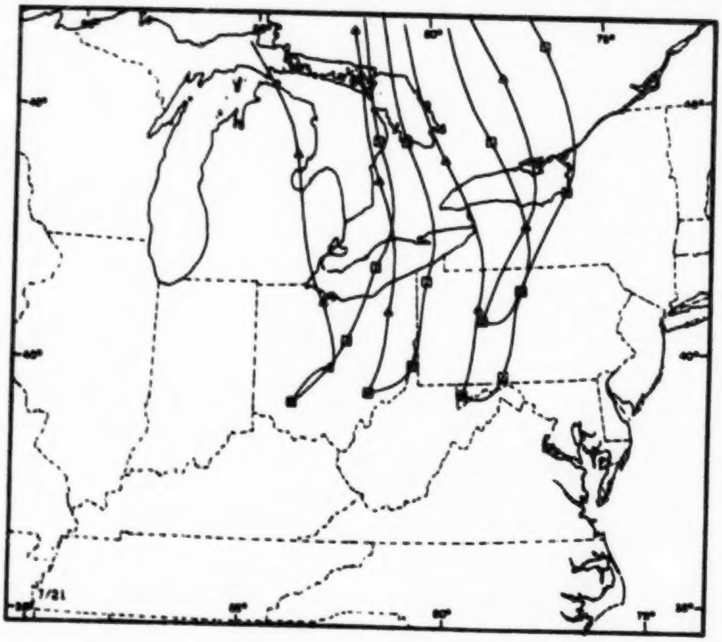

7/16
85°
80°
75°
35°

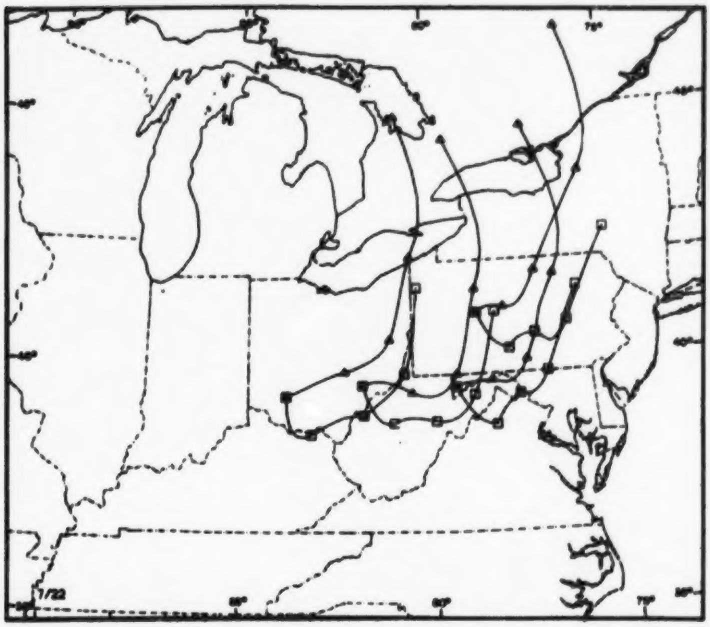

7/17
85°
80°
75°
35°


7/18

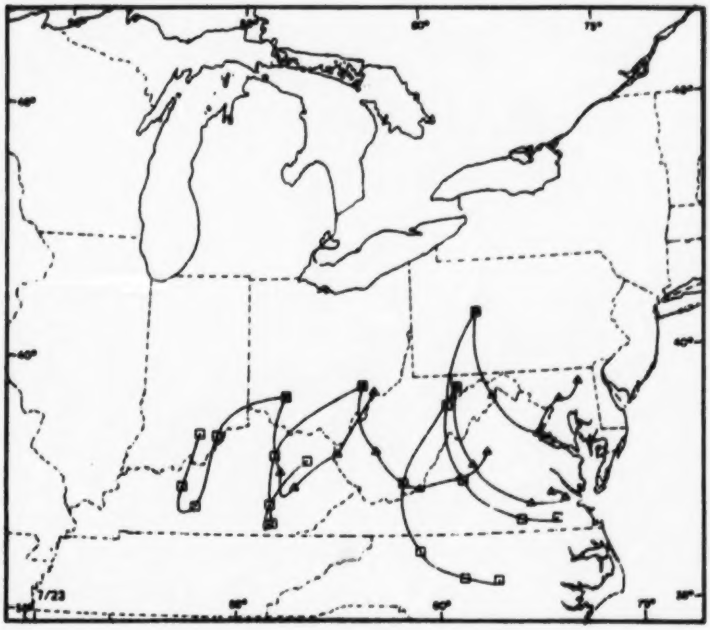

7/19


7/20

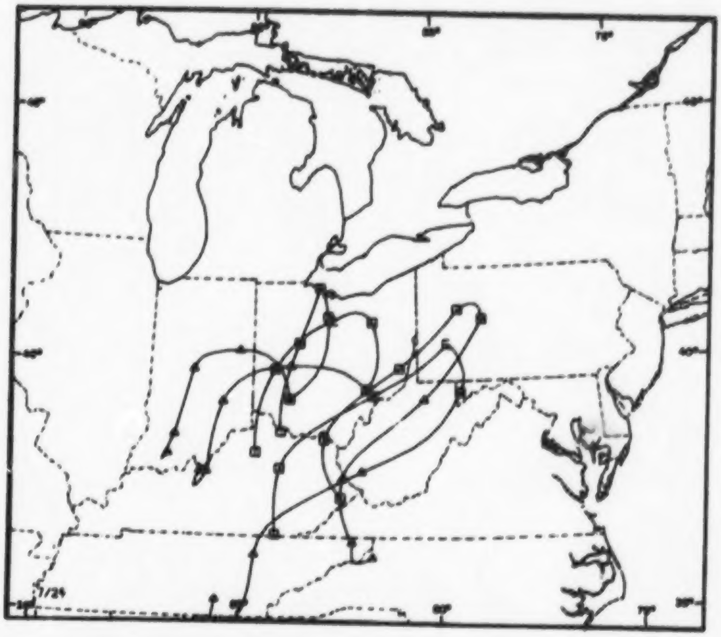

7/21

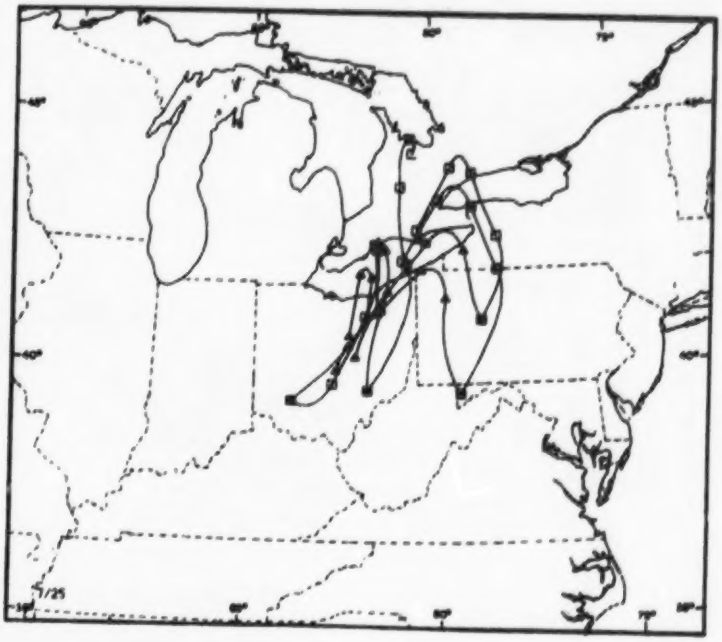


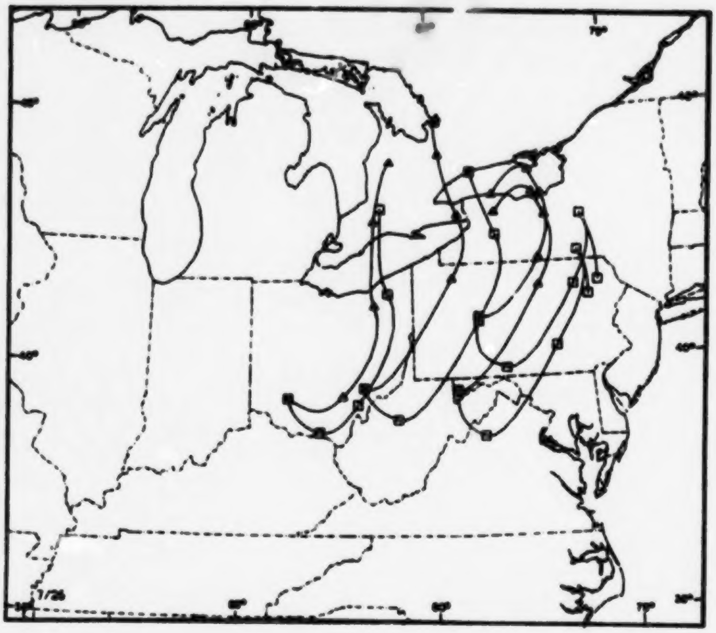
85°
80°
75°
45°
40°
35°
7/22

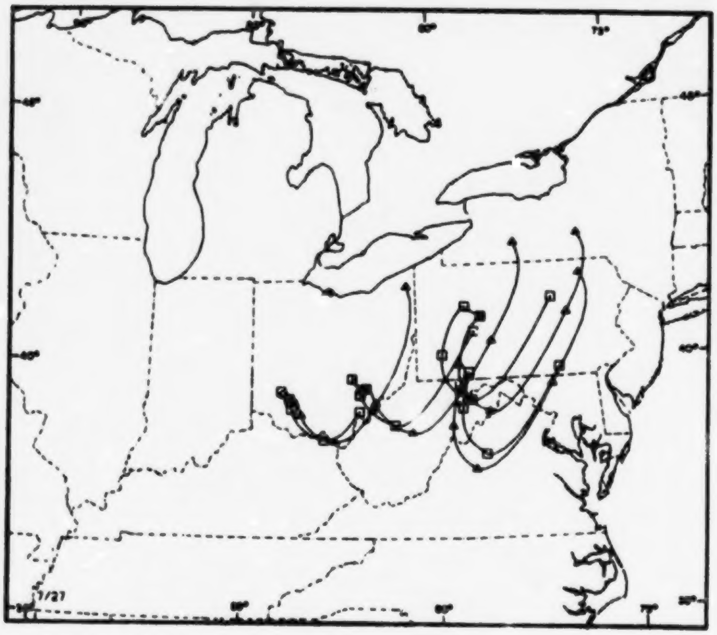


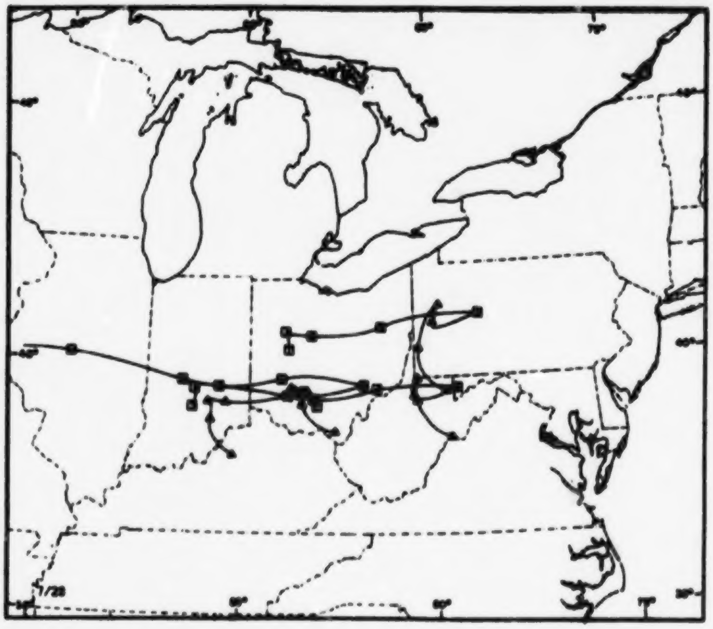
85°
80°
75°
45°
40°
35°
7/23

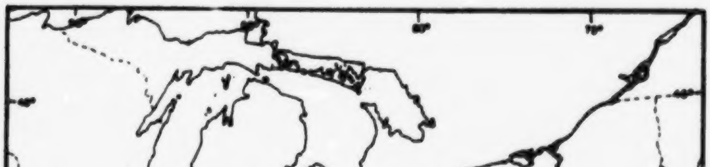

1/24

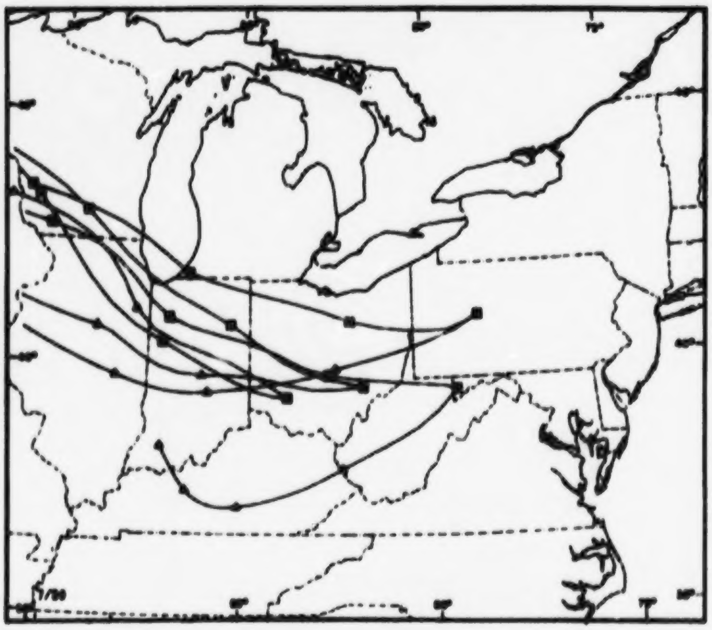

1/25

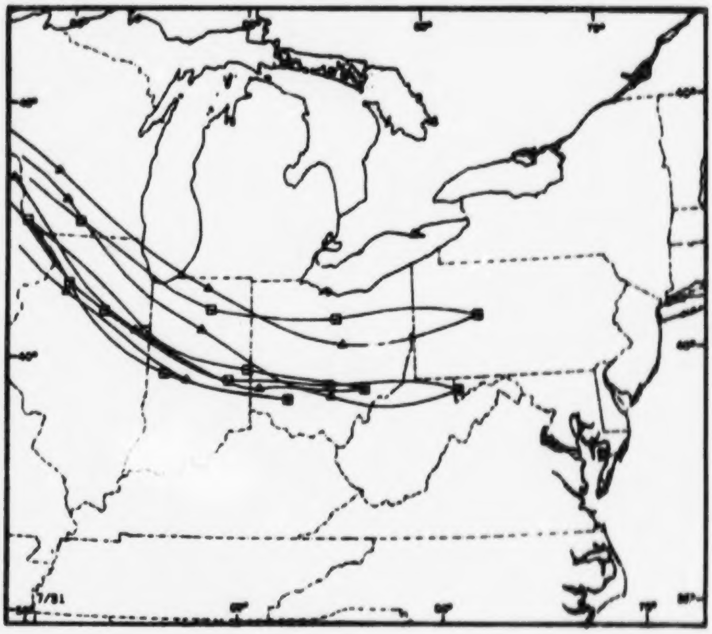

7/26

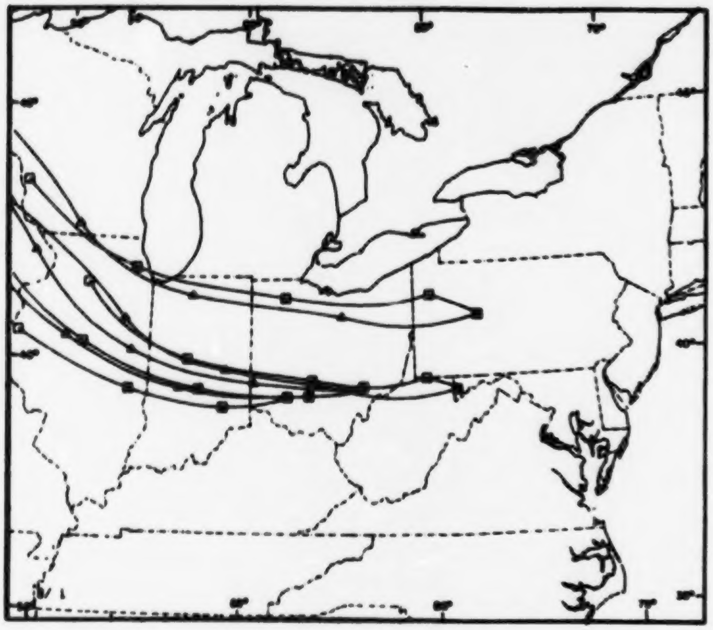

7/27

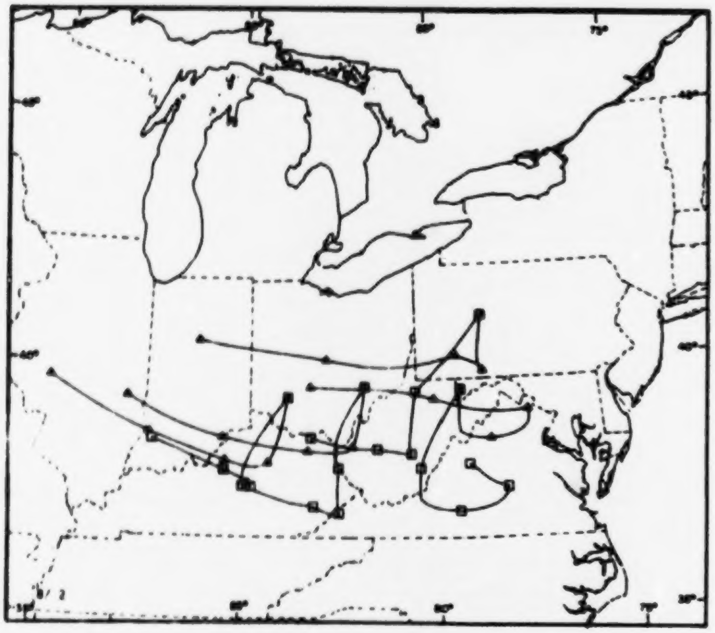

90°
80°
70°
40°
7/29
35°

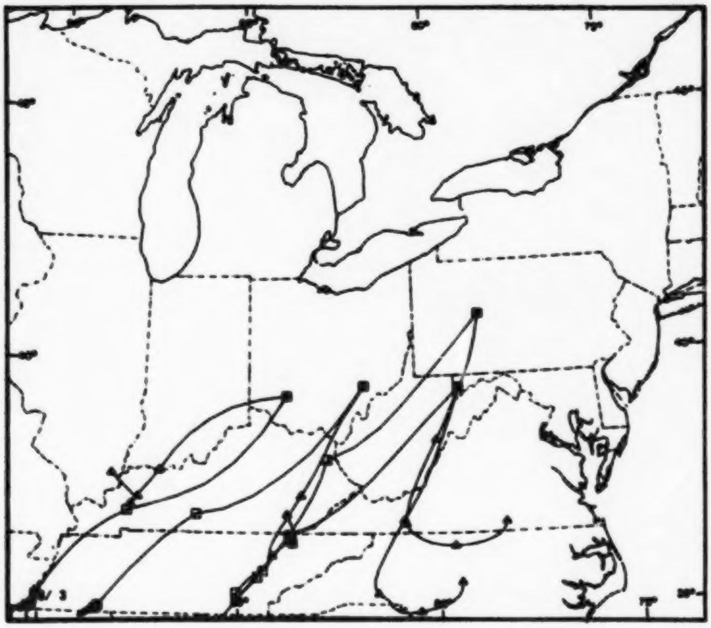

90°
80°
70°
40°
7/29
35°

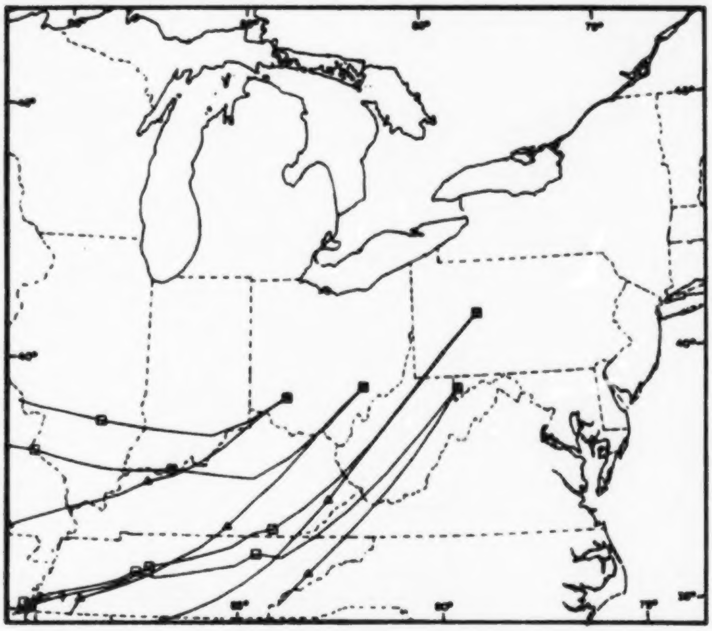

7/30

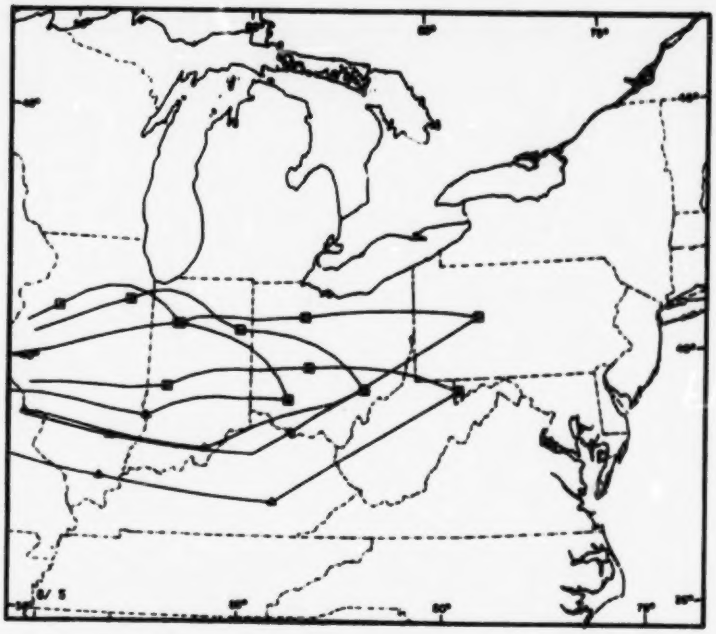

7/31

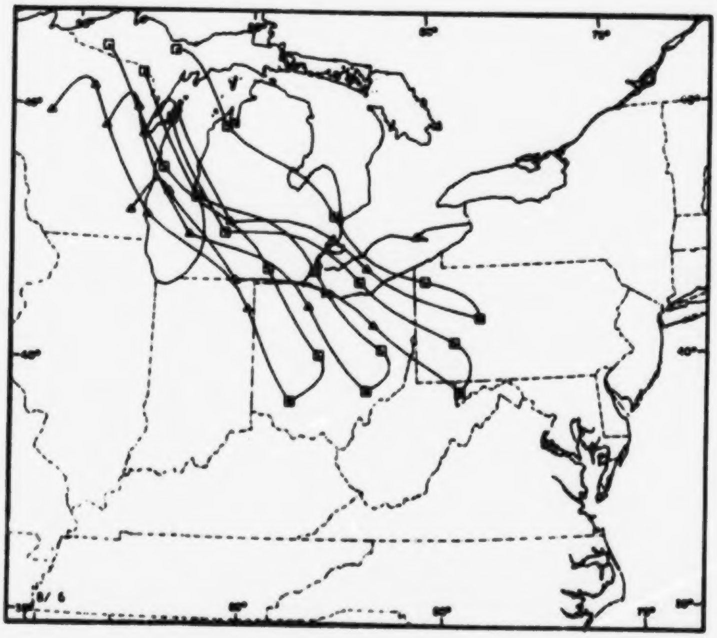

8/ 1

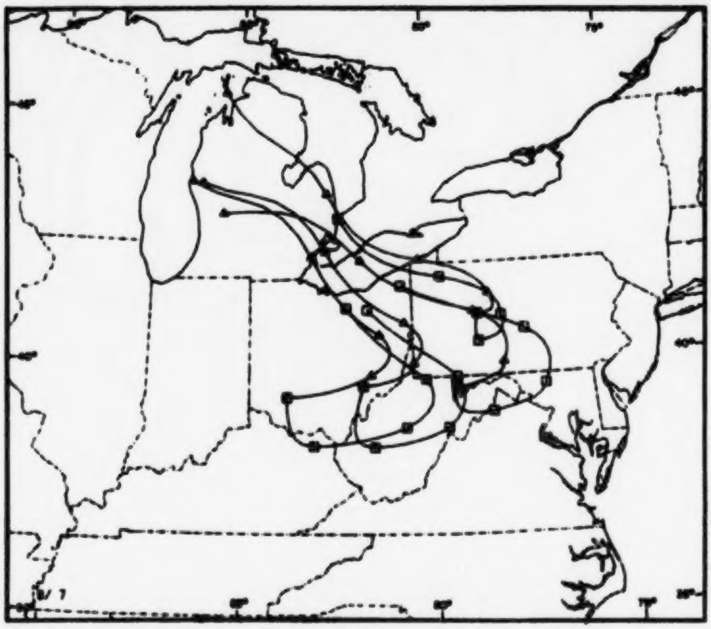

8/ 2



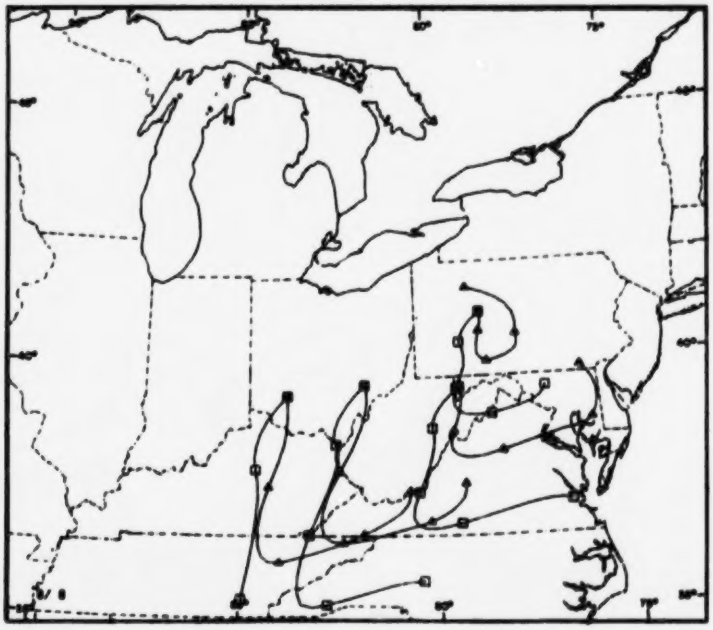



8/ 5

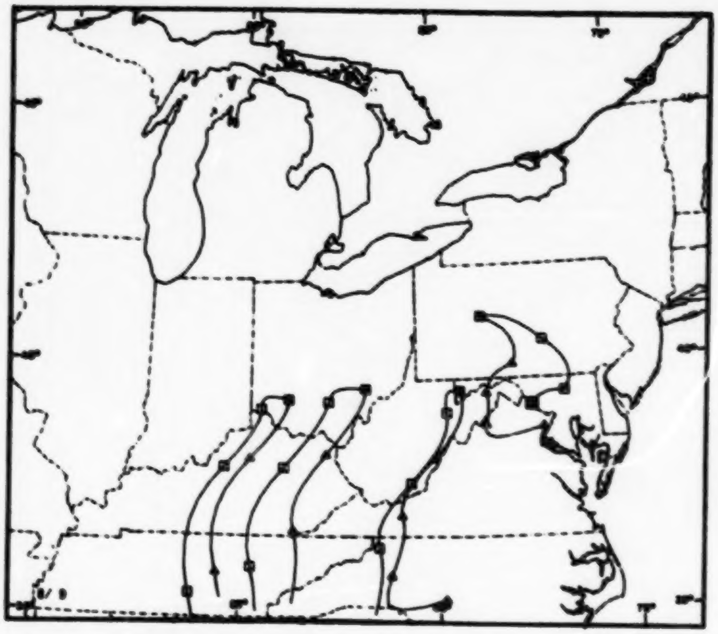

8/ 6

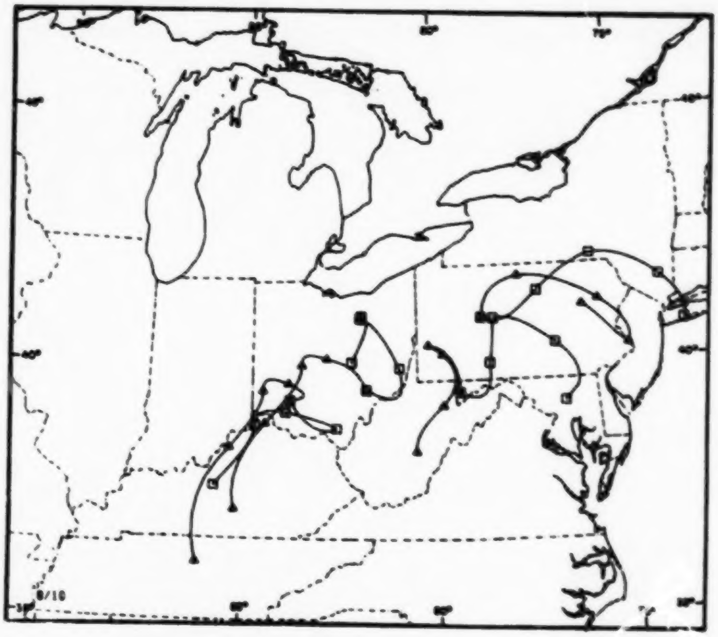


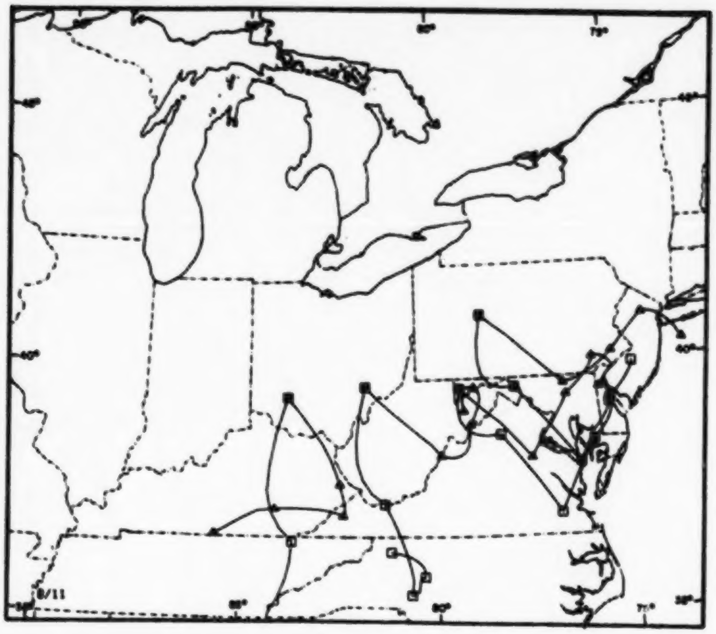
80°
75°
5/ 7

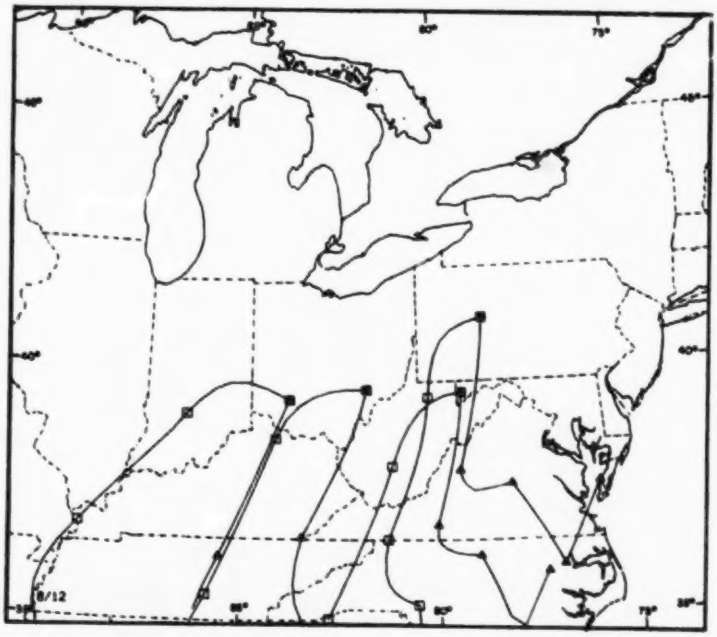


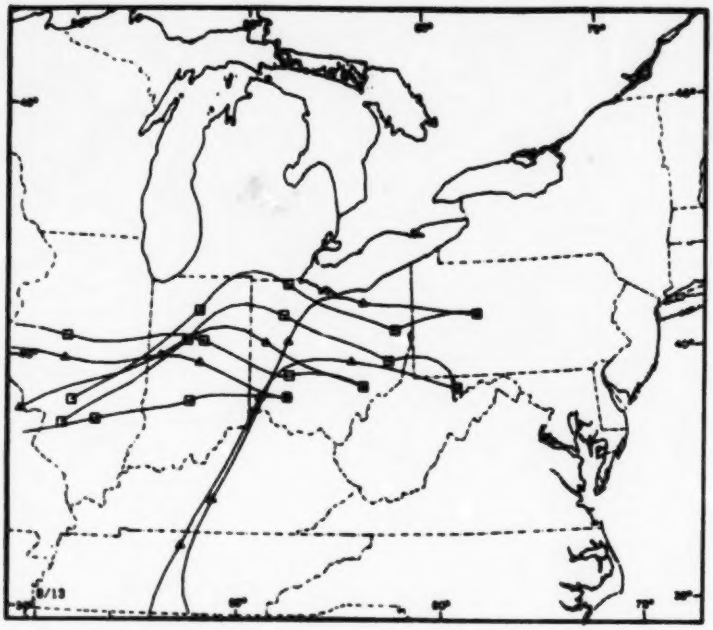
80°
75°
5/ 8


8/ 9

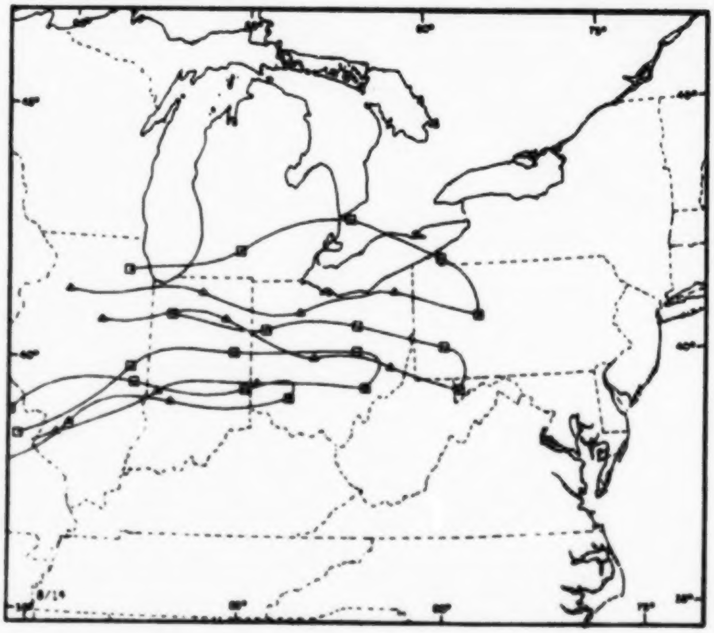

8/10


8/11
80°
75°
85°
45°
40°
35°

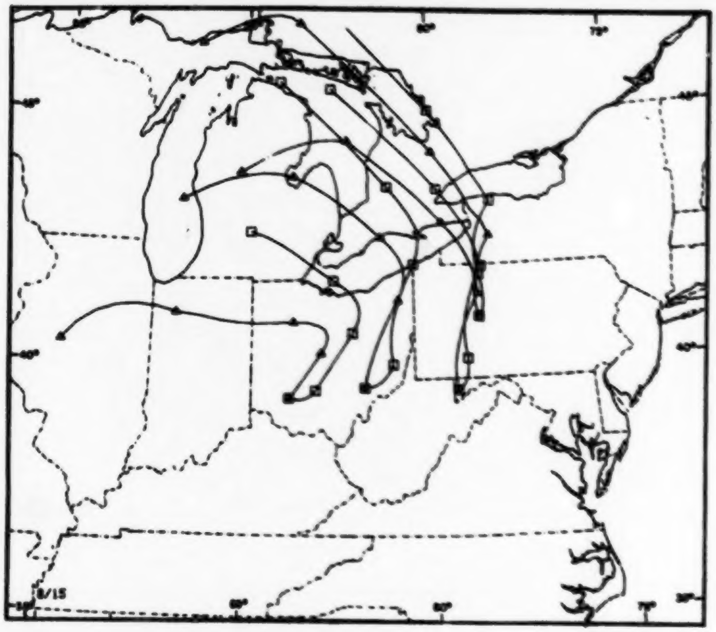

8/12
80°
75°
85°
45°
40°
35°

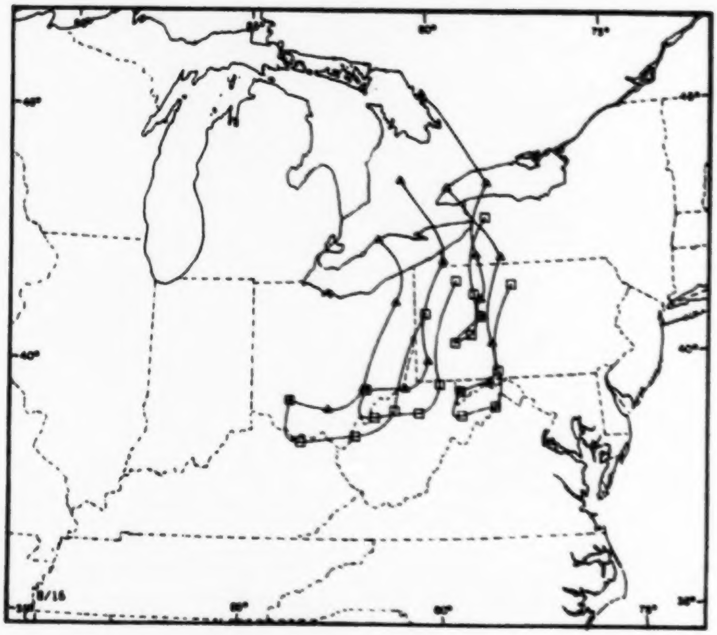


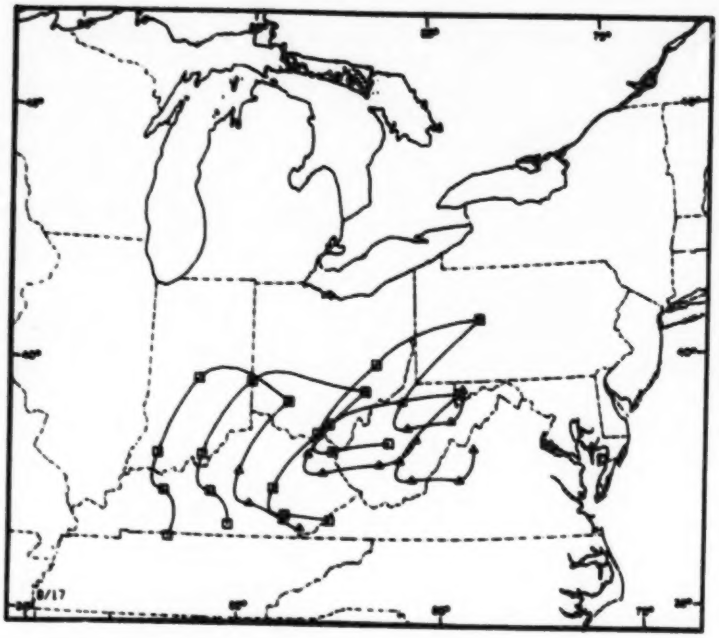
8/13

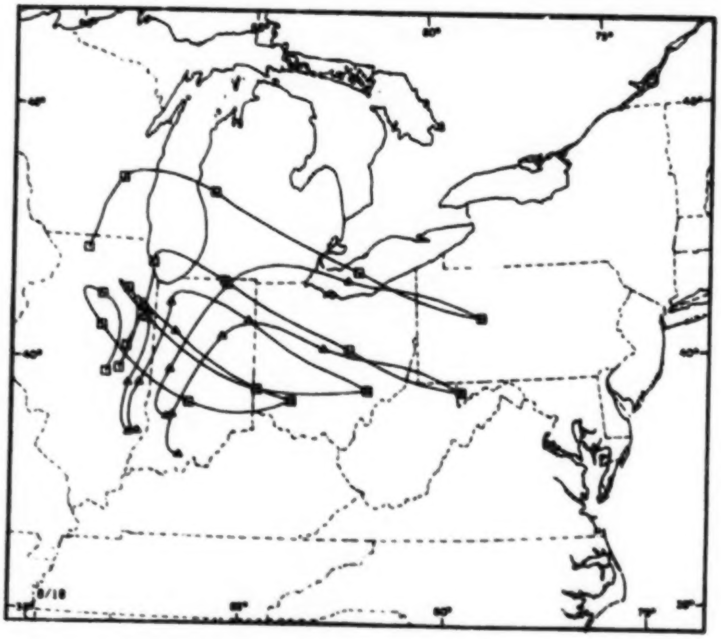


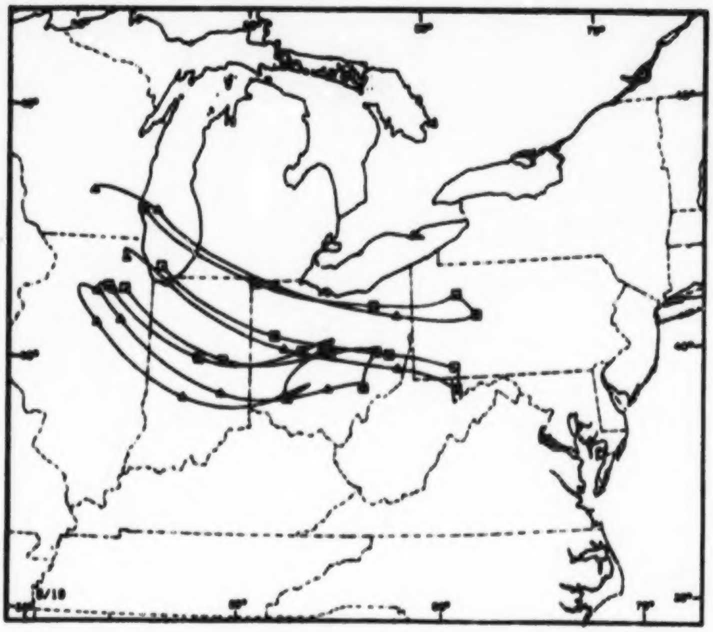
8/14


80°
75°
45°
40°
8/15
35°
85°
80°
75°
35°

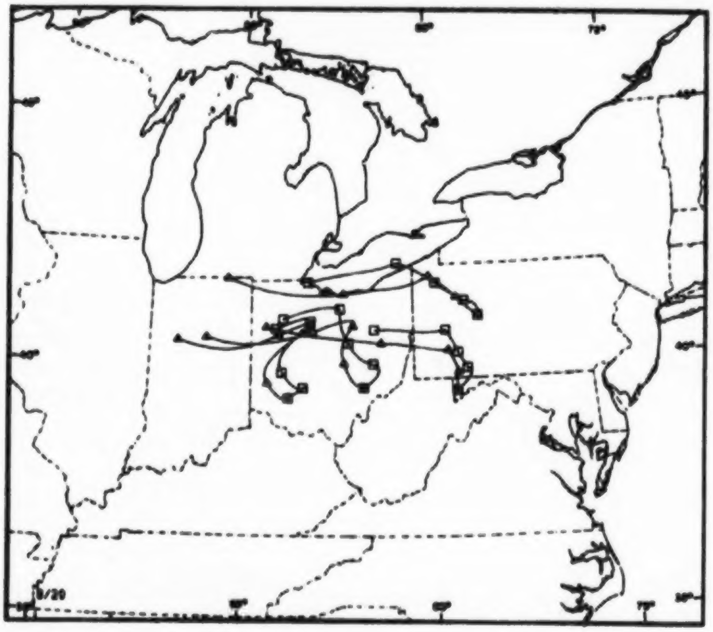

80°
75°
45°
40°
8/16
35°
85°
80°
75°
35°


80°
70°
8/17

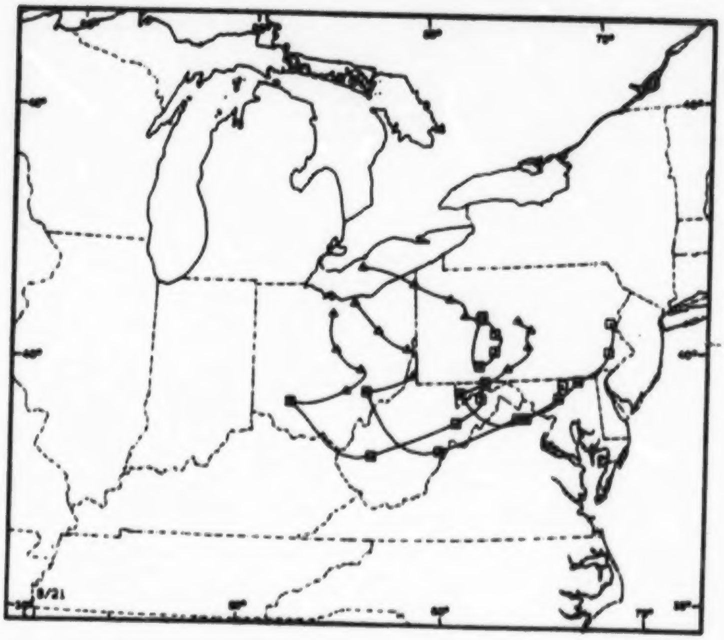

80°
70°
8/18

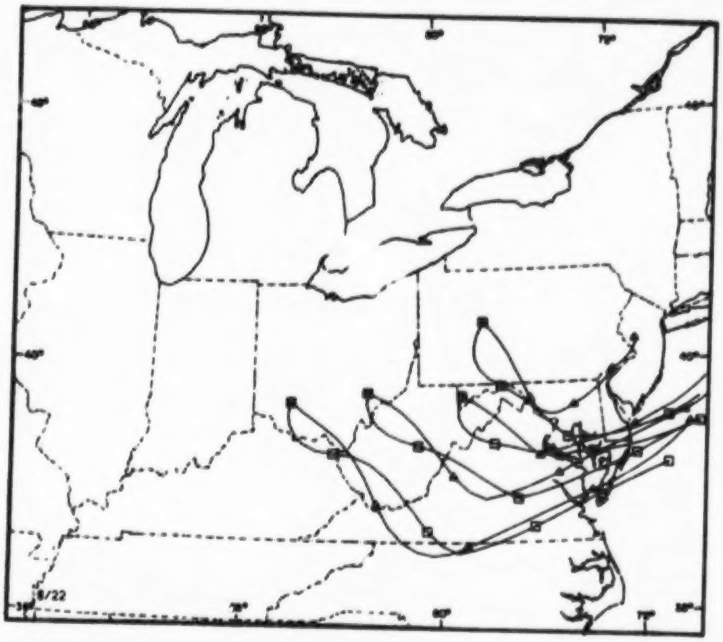


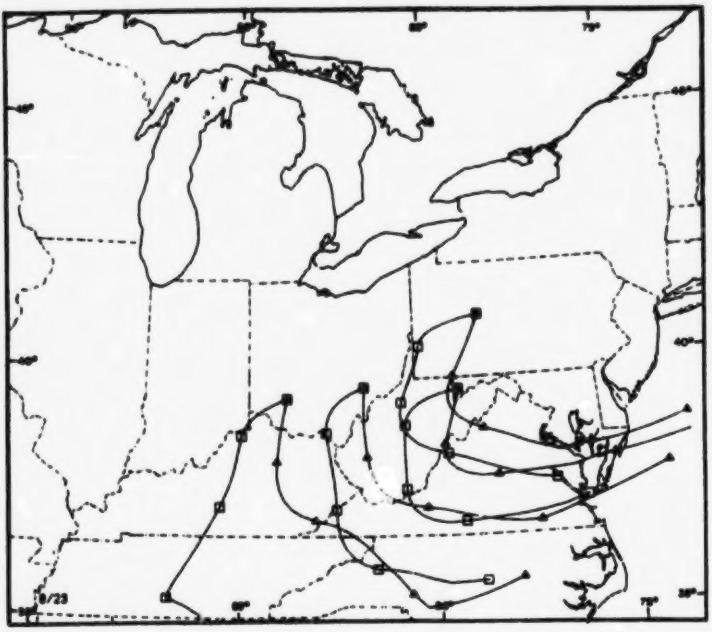
5/19
85°
80°
75°

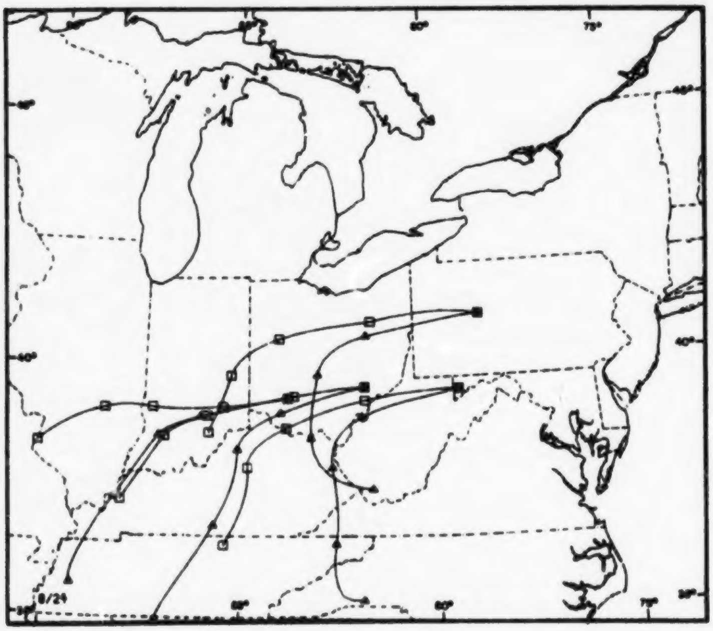


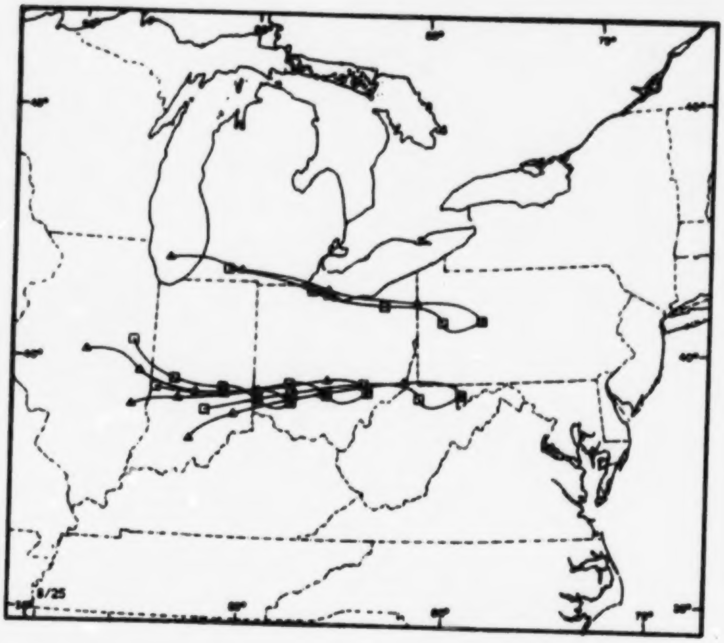
5/20
85°
80°
75°


8/21

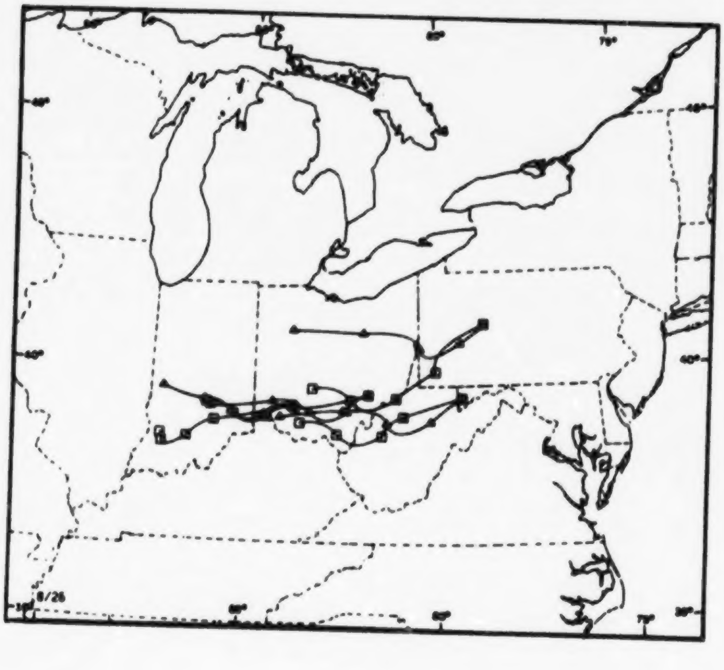

8/22


85°
80°
75°
45°
40°
35°
8/23

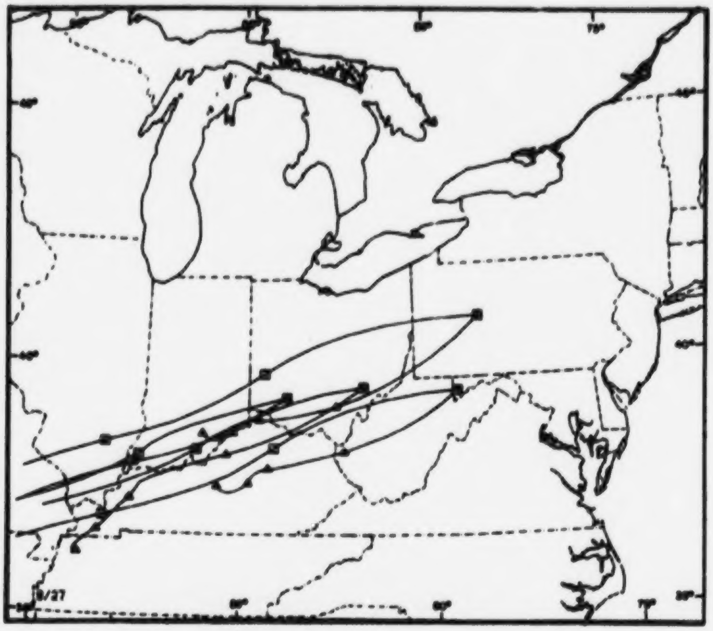

85°
80°
75°
45°
40°
35°
8/24

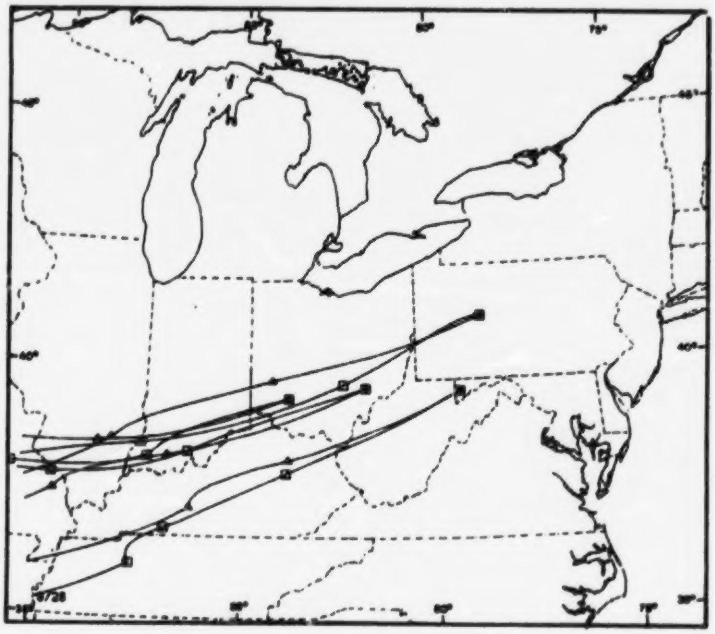


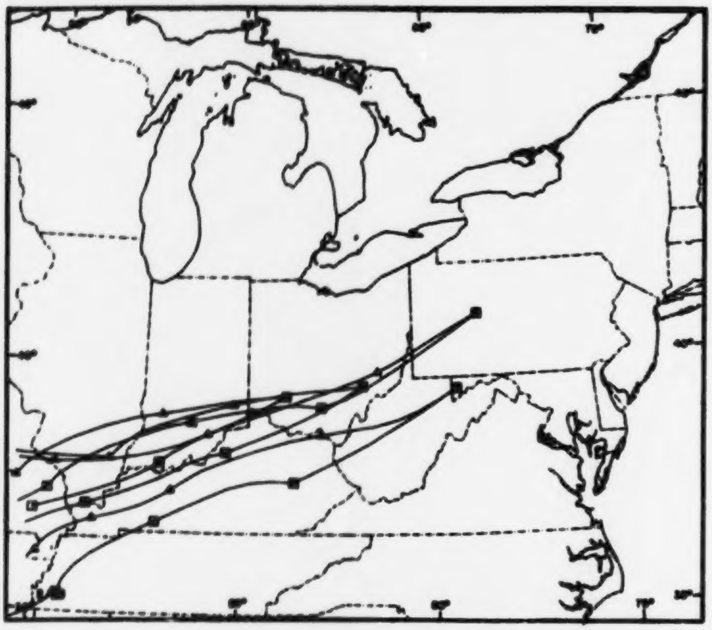
8/25

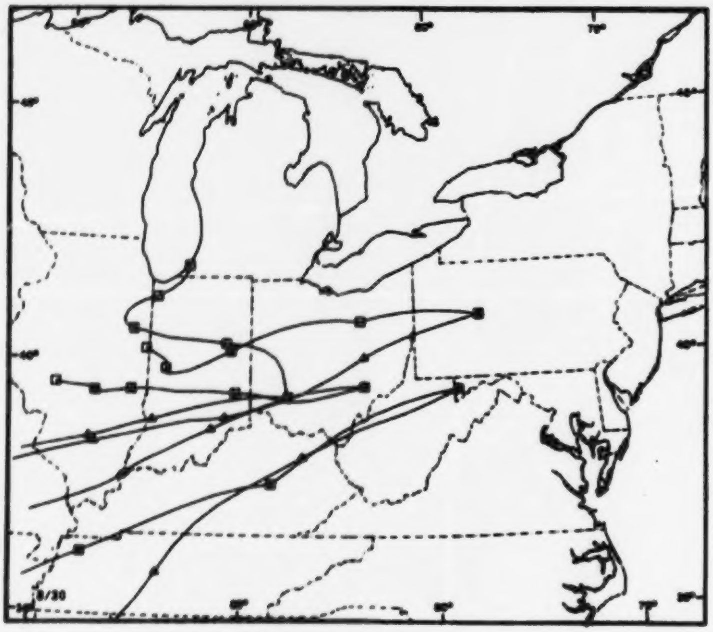


8/26

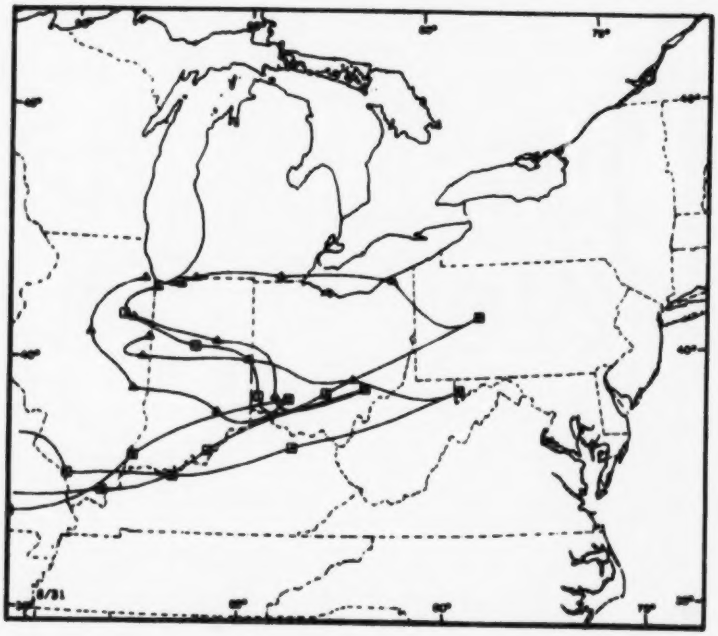

80°
70°
40°
30°
8/27


80°
70°
40°
30°
8/28

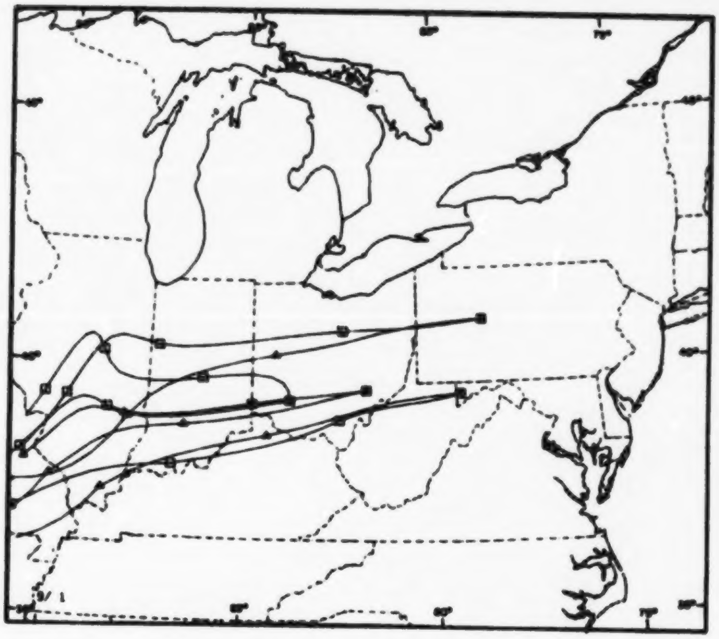




8/30



8/31



9/ 1